Some Unique Management Characteristics of Residues from Atmospheric Fluidized-bed Combustion

Report EPS 3 PG 10
June 1987

Environment CANADA Environnement
2039102K VOL 3PG ISS 10 870600
EXC # 001
TD 182 R46
REPORT (CANADA. ENVIRONMENT CANADA)

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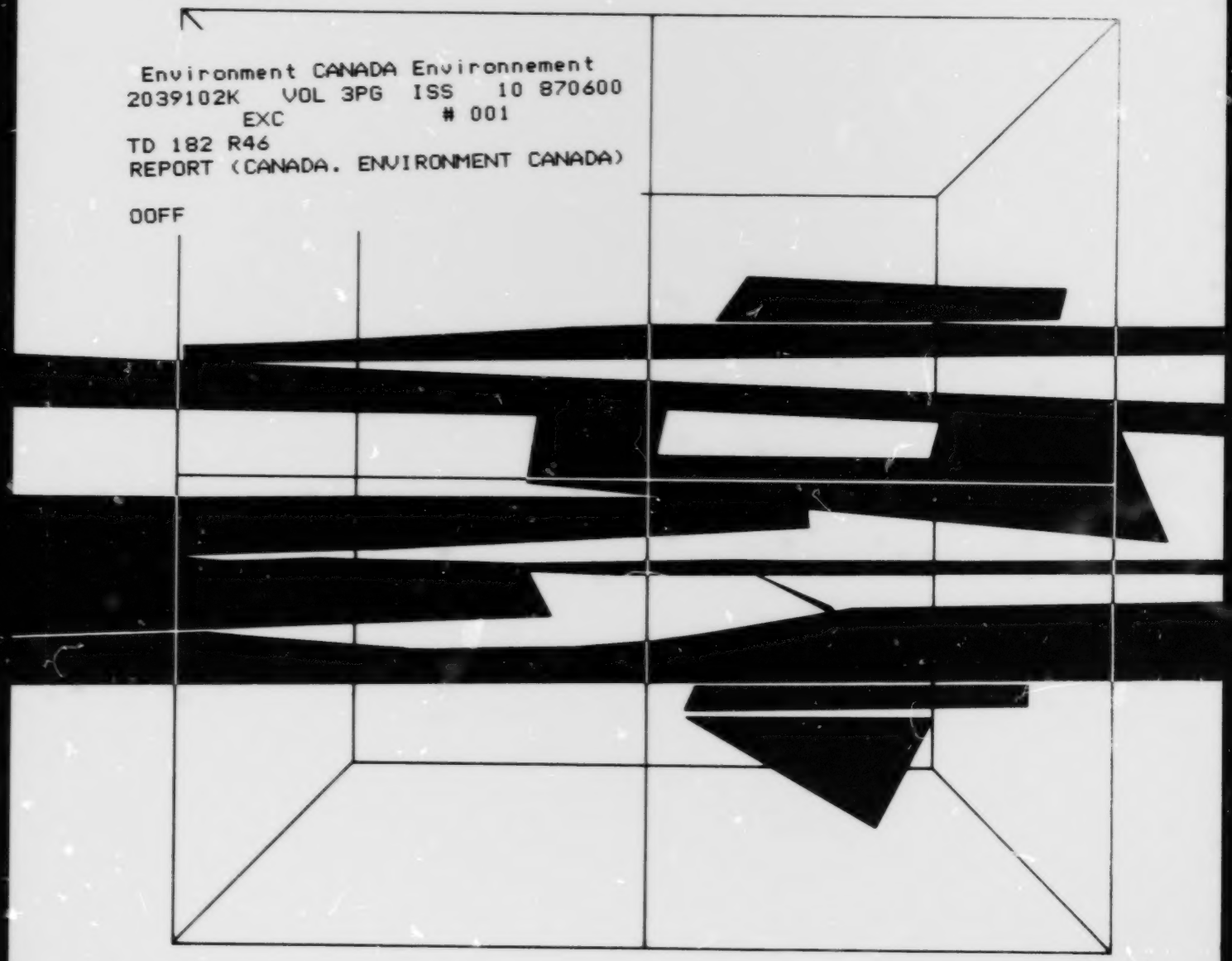

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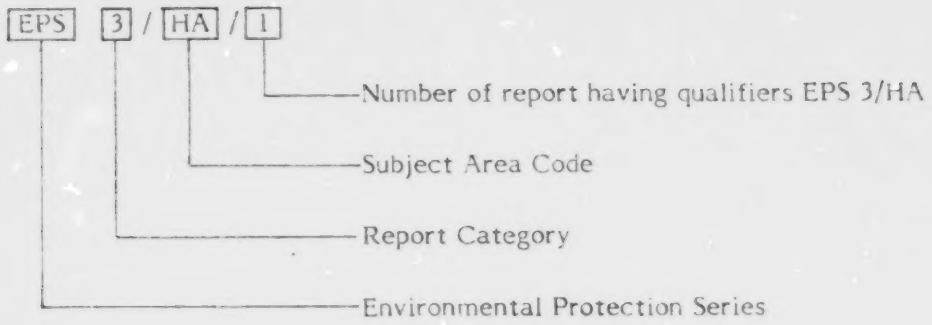

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SOME UNIQUE MANAGEMENT CHARACTERISTICS OF RESIDUES FROM ATMOSPHERIC FLUIDIZED-BED COMBUSTION

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Report EPS 3/PG/10
June 1987

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Cat. No. En 49-9 3-10E
ISBN 0-662-15477-0
BEAUREGARD PRESS LIMITED

ABSTRACT

Atmospheric fluidized bed combustion (AFBC) technology for solid fuels is under rapid development around the world. One major impetus is the quest for reduced polluting emissions into the air during the combustion of low-quality coals. Other incentives include simplicity of design, construction, and operation as well as the potential to retrofit or repower existing installations at reasonable cost.

Several different fluidized bed combustor designs are under development. The most widely tested on bench-and pilot-scale, and in demonstration units is the bubbling bed design.

The characteristics of the solid wastes from bubbling bed combustion are also under study to develop environmentally and economically optimal systems for waste collection, handling, transport, and disposal systems. Some waste characterization information may also be of benefit for refinement of the combustion technology itself.

In this study, results of previous waste studies are re-evaluated on the basis of observations made at operating AFBC units. The observations focussed on ascertaining whether particular characteristics indicated in laboratory work were factors in day-to-day operations. The laboratory results and field observations were then synthesized and used to develop outlines for practicable waste handling and disposal as well as to identify remaining problem areas which might require further study. Several potential concerns involving crystalline calcium oxide content and the effects of calcium oxide content on physical characteristics including exothermic reactions of the wastes were examined. However, no potential problems were identified which could not be overcome through the continued development of operational practices and technologies which took these characteristics into account.

RÉSUMÉ

La technique de la combustion atmosphérique sur lit fluidisé (AFBC) connaît un développement rapide partout dans le monde. L'un de ses principaux avantages réside dans la réduction directe des émissions de polluants au cours de la combustion du charbon de mauvaise qualité. Parmi les autres attraits de la technique, on note la simplicité de conception, de construction et de fonctionnement de même que la possibilité de procéder au rattrapage ou à la réactivation d'installations existantes à un coût raisonnable.

Plusieurs sortes d'appareils de combustion sur lit fluidisé sont en train d'être mis au point, mais le type à bulles semble le plus utilisé jusqu'à maintenant dans les essais et projets de démonstration.

Les caractéristiques des résidus solides de la combustion sur lit fluidisé à bulles sont aussi étudiées afin de concevoir des méthodes de collecte, de manipulation, de transport et d'élimination des résidus optimales sur les plans environmental et économique. Certains renseignements reliés à la caractérisation de ces résidus pourraient aussi permettre d'améliorer les techniques de combustion.

La présente étude a permis de réévaluer les résultats d'études antérieures sur les résidus et de visiter des unités de combustion atmosphérique sur lit fluidisé en exploitation afin d'observer si certaines caractéristiques mentionnées dans les études en laboratoire pouvaient influer sur leur marche quotidienne. La synthèse des résultats obtenus en laboratoire et des observations sur place a servi à la conception de méthodes pratiques pour la manutention et l'élimination des résidus ainsi qu'à la détermination d'autres aspects perfectibles à étudier. C'est ainsi qu'on a examiné l'effet de la teneur en oxyde de calcium à l'état cristallin sur les caractéristiques physiques des résidus, y compris les réactions exothermiques de ces derniers. Ces travaux n'ont toutefois pas permis de découvrir des problèmes impossibles à surmonter par la mise au point continue de méthodes et de techniques qui tiennent compte de ces caractéristiques.

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1 INTRODUCTION

1.1 The Advantages of AFBC

The technology of coal-fuelled atmospheric fluidized-bed combustion (AFBC) has undergone rapid development in Canada and elsewhere through extensive pilot-plant and demonstration-scale combustor testing, to the point where it is now being widely considered for a variety of industrial applications. This technology has a major advantage: it can reliably burn coals of varying quality and high sulphur content interchangeably and still achieve large reductions in sulphur dioxide and nitrogen oxide air emission. Simplicity of design, construction, operation of air emissions control mechanisms and the potential to retrofit or repower existing stations are other attractive advantages.

Since SO_x and NO_x emissions are significant contributors to acid rain formation, from the perspective of environmental protection, the simple, yet effective, sulphur and nitrogen oxides emission reduction features of this technology, even for coals of high sulphur content, are a real boon. However, the retention of potential atmospheric pollutants in the solid combustion residues and the addition of the sulphur capture materials increase the amount of combustion-related solid wastes. The solid residues generated in this process have some properties different from the combustion wastes of conventional pulverized coal. These properties can affect waste management and disposal.

Because of the potential for generation of large volumes of AFBC wastes, a number of investigations of these wastes have been conducted. For example, the U.S. Environmental Protection Agency (1) and the U.S. Electric Power Research Institute (2) have undertaken projects aimed at studying the characteristics of these combustion residues and how the characteristics affect leachability. Other studies conducted by Environment Canada have emphasized properties relating to residue handling and disposal, as well as the chemical and leaching properties of residues from the combustion of high-sulphur Canadian coal with Canadian limestone.

As AFBC technology evolves toward widespread industrial use, practical handling and disposal technologies must be developed to avoid any potential problems with this type of residue. Understandably, data on existing designs with such technologies are very limited to date. For that matter, regional North American (or European) experiences may be of limited applicability in Canada because of the unique coals, emission standards,

and climatic patterns. For example, in eastern Canada, information from the western U.S.A. may be of limited application.

1.2 Objectives

This investigation is directed at the identification of potential problems in the handling, and disposal, of AFBC combustion residues in Canada. The practical aspects and bulk properties of the residues, which might require special refinement in safe collection, handling, and disposal are emphasized. This approach represents the next step in the assessment and development of AFBC technology, and hopefully will expedite its progress from demonstration scale to full scale. Previous investigations have indicated that a potential for some unusual problems may exist. Therefore the specific objectives of this study are:

- To document and evaluate the unique properties of AFBC residues.
- To document and evaluate any problems which have been encountered with the handling and disposal of AFBC residues.
- To summarize the basic theory describing exothermic reactions in solid materials, and to describe the properties of coal-fired AFBC residues in terms of a thermodynamic relationship.
- To outline practical handling and disposal methods for wastes of this type, which would be applicable in operations on the scale likely to be encountered in Canada.
- To identify gaps in knowledge about the properties of this type of waste and about its disposal, and recommend appropriate further studies to promote the development of more precise waste management techniques.

2 SUMMARY OF PUBLISHED INFORMATION

2.1 Introduction

This section summarizes existing published information on the potentially hazardous properties of bubbling bed AFBC residues. The summary identifies particularly those properties important in handling and disposal practices. For example, a large body of data exists on the formation and properties of single AFBC particles. In this report, however, the emphasis is on the properties of residue in bulk, and therefore an observational rather than a theoretical approach has been taken. Similarly, the North-American experience to date has been primarily with AFBC units of the bubbling bed-type, and emphasis is on these. New, larger circulating bed-type units are being introduced but their waste characteristics are expected to differ somewhat from those described here. Four properties considered to be unique to the type of combustion residue are:

- particle size (dusting),
- chemical composition (leachability),
- chemical reactivity (heat or fast reaction problems), and
- engineering characteristic (secure disposal area design).

2.2 Particle Size

The particle size distribution of AFBC residues can influence a number of other widely different properties and concerns in waste handling and disposal. For example, the size of the particles may determine the geotechnical properties (e.g., compactability and drainage) of the residues; the waste may be dusty, causing concerns for human health, environmental protection, and equipment maintenance. The presence of fine, non-wettable particles may also lead to wind-borne erosion and fugitive dust emissions at the disposal site.

2.2.1 General. Typically, particle size distributions are determined by using sieve analysis. However, this technique is limited to particles that cannot pass U.S. sieve number 400 or 0.037 mm (0.0015 inch). For particles smaller than 0.037 mm, hydrometer analysis is often used. A limitation of the hydrometer method for AFBC residues is that the wastes may react chemically on contact with water. This reaction may produce smaller particles and bulk swelling or size instability. Technically more sophisticated methods, including light and electron microscopy and particle impactors, are now available to size particles in the micron range, but equipment availability and cost may limit their use.

2.2.2 Relevant Data. Collins (3) examined the particle size of wastes from five AFBC combustors. All particles ranged in size from about 0.1 mm to 10 mm; 50 percent of the residue passed through the 1.0 mm mesh. This distribution is similar to that of coarse sand. Eklund and Wellington (2) reported a particle size distribution and particle size analysis for residues from the Alliance bubbling AFBC test facility. This data, shown in Figures 1 and 2, includes both sieve and hydrometer analyses. The particle size analysis for this waste indicates a trimodal distribution:

Particle Size (mm)	Distribution (%)
0.71	19
0.44	41
0.009	30

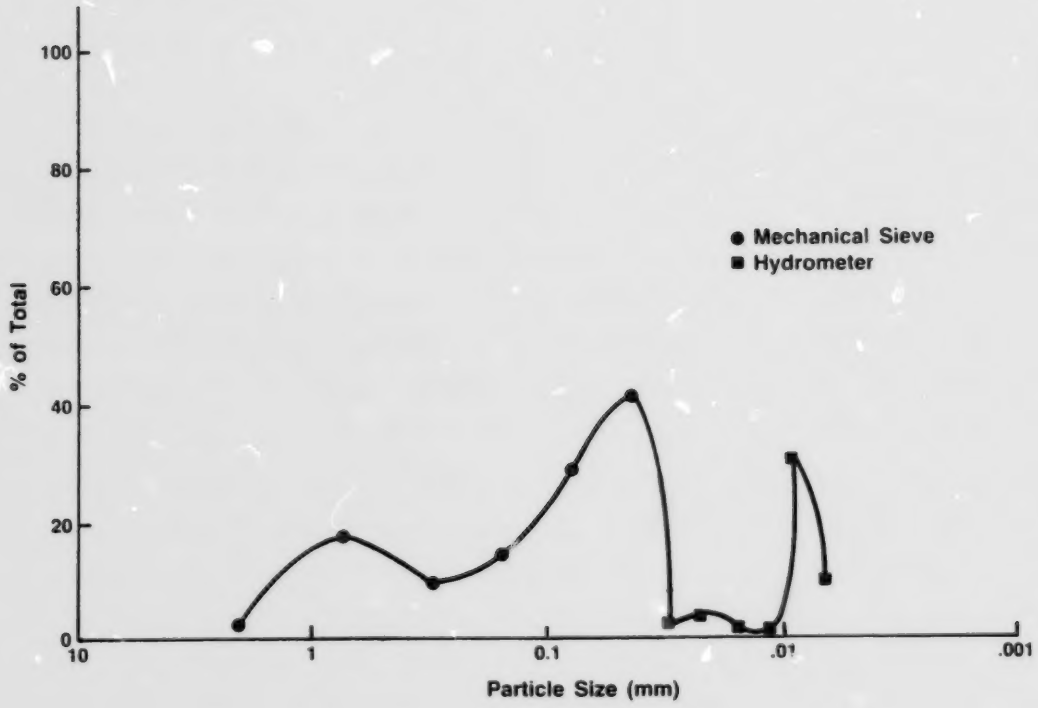


FIGURE 1 PARTICLE SIZE DISTRIBUTION (2)

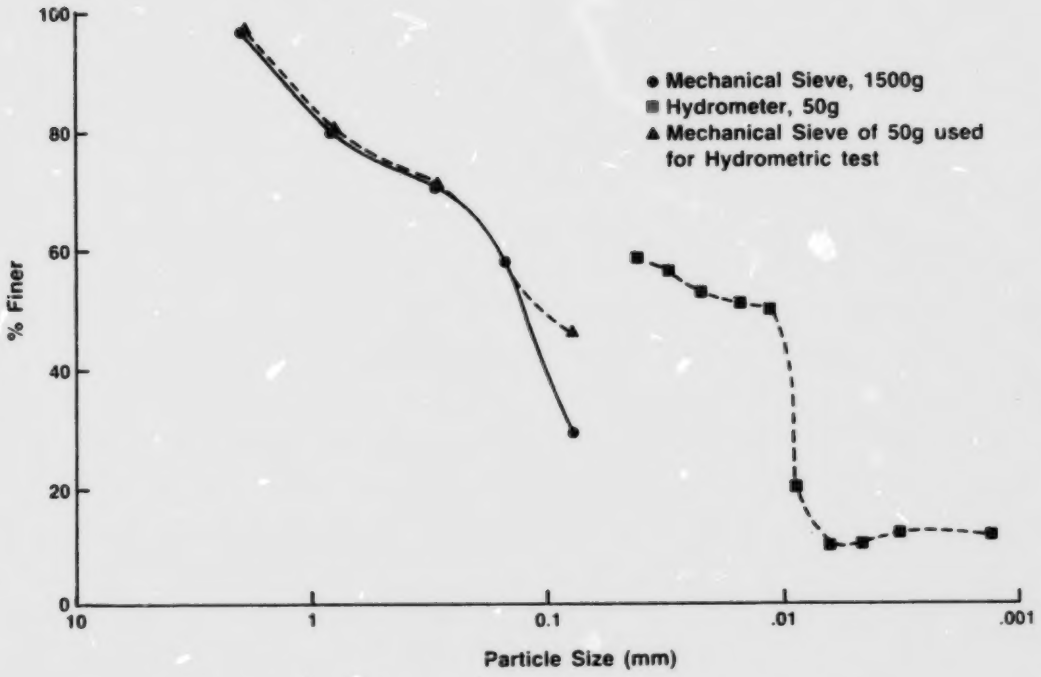


FIGURE 2 PARTICLE SIZE ANALYSIS (2)

The baghouse ash (fly ash or carryover) contributes almost 70 percent of the particles 0.125 mm or smaller in diameter. These are in the size range of silt-clay particles. However, the reliability of sizing by hydrometer is questionable, due to the potential for reaction of the waste with water.

Stone and Kahle (4) presented particle size analyses of both slaked and unslaked spent bed and fly ash (Figures 3 and 4). Slaking clearly reduces the particle size bed material. For example, of the unslaked bed material about 5 percent is less than 0.5 mm in diameter, whereas of the slaked residue, about 40 percent is finer. But slaking does not appear to change the particle size distribution for fly ash.

Dearborn (5) determined the particle size distribution of unslaked spent bed and carryover residues from the combustion of high-sulphur eastern Canadian coal and limestone. Two bed materials tested ranged in size from 0.1 to 20 mm, with 50 percent passing through a 1.0-mm mesh, similar to coarse sand in particle size. Through hydrometer analyses, fine particles, ranging from 0.001 to 0.1 mm in diameter, were found in the slaked spent bed material.

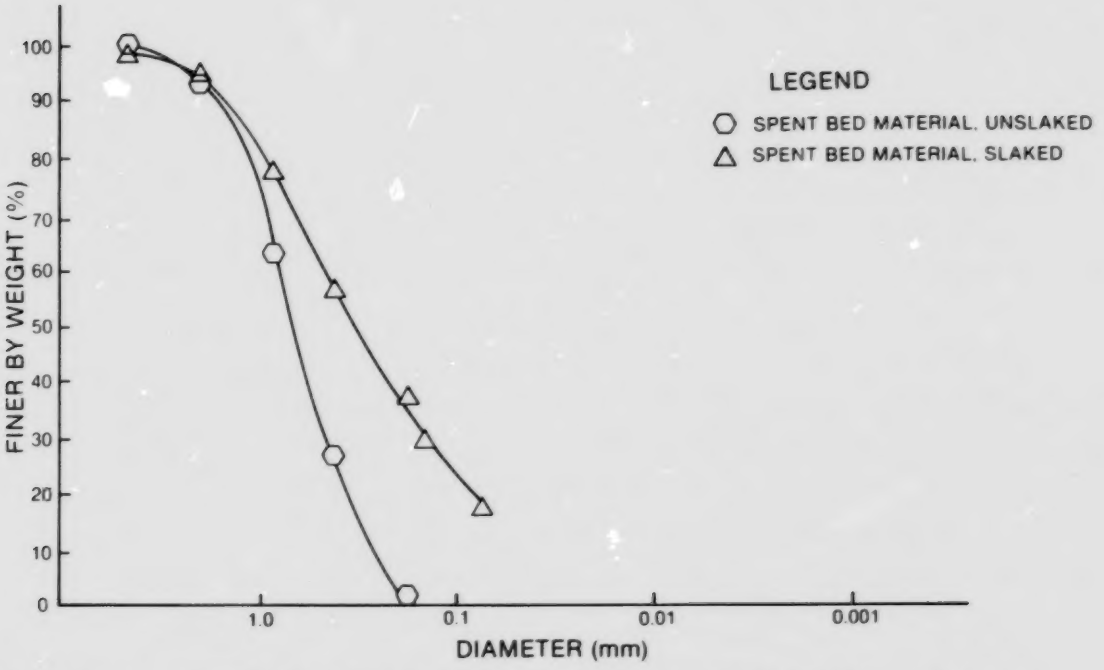


FIGURE 3 PARTICLE SIZE ANALYSIS OF SPENT BED MATERIAL (4)

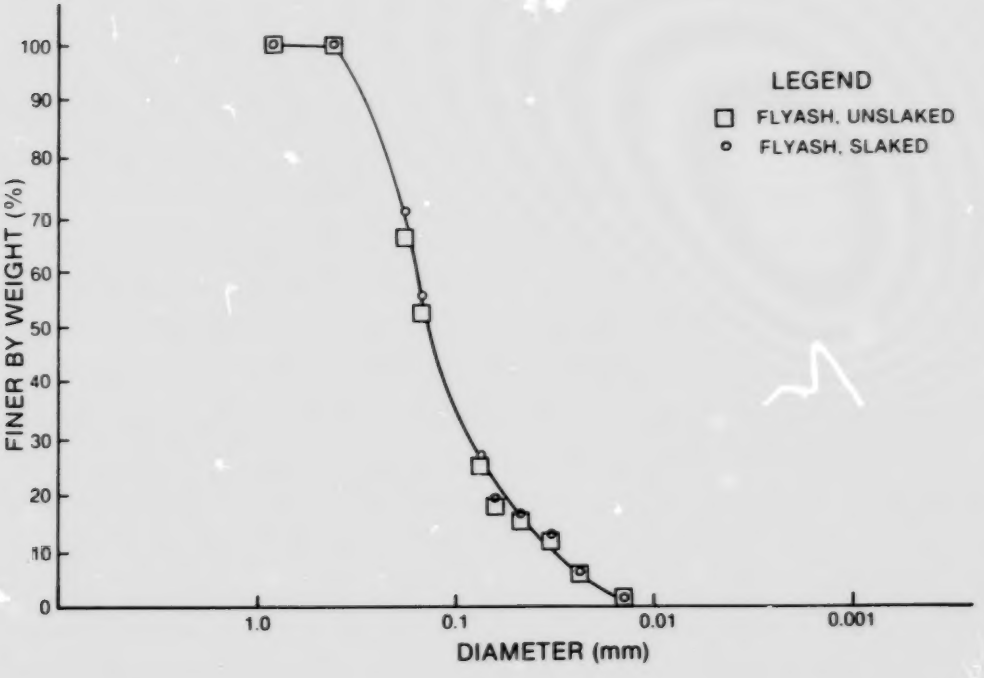


FIGURE 4 PARTICLE SIZE ANALYSIS OF CARRYOVER (4)

For the (unslaked) carryover material, particle size ranged from 0.1 to 0.5 mm in diameter with 50 percent passing through a 0.09-mm mesh. This is about one-tenth the diameter of the unslaked bed material. Through hydrometer analysis of slaked samples, fine particles, ranging from 0.001 to 0.04 mm in diameter, were found.

Hobbs (6) summarized in-stack particle sampling studies conducted by several researchers. Cascade impactors were used to determine particle distributions, and mass median aerodynamic diameters (MMAD) were calculated. Table 1 summarizes the aerosol size and mass concentration of particles in an experimental FBC exhaust stream combusting coal with limestone (7). The sampling and analysis indicate the presence of respirable aerosols in the stack breach; that is, particles in the range of 2.2 to 2.8 μm MMAD. For comparison, Figure 5 shows the deposition of particles by mass median diameter in the various passages in the human respiratory system (8). A comparison of the Table 1 and Figure 5 suggests that particles produced by AFBC units may be sufficiently small to penetrate deep into the human respiratory system.

TABLE 1 SUMMARY OF AEROSOL SIZE AND MASS CONCENTRATION AT VARIOUS LOCATIONS IN AN EXPERIMENTAL FBC EXHAUST STREAMS FOR DIFFERENT FUELS

		Sampling Position			
Coal Type	Parameter Measured	Stack Breach	Baghouse Inlet	Between Cyclones	Top of Combustor
Montana Rosebud	MMAD (a)	2.3 x 0.3	2.3 x 0.2	2.2 x 0.1	3.9 x 0.8
	g/m^3 (b)	7.0×10^{-2}	0.38	1.2	4.7
Montana Rosebud II	MMAD	2.4 x 0.2	3.0 x 0.4	2.7 x 0.3	6.1 x 0.9
	g/m^3	3.0×10^{-2}	0.56	0.59	3.4
Texas lignite I (bulk)	MMAD	2.8 x 0.3	3.2 x 0.4	3.0 x 0.3	4.8 x 2.3
	g/m^3 (c)	1.8	3.1	3.2	
Western Kentucky	MMAD	2.5 x 0.2	3.0 x 0.4	2.7 x 0.3	5.4 x 1.1
	g/m^3	2.0×10^{-2}	0.46	0.42	3.4
* Operating conditions:	790-940°C mid-bed combustion temperature 0.9-1.4 m/s fluidized velocity				

(a) Mass medium aerodynamic diameter, micrometers (geometric standard deviation ranges between 1.6 and 2.1 for all cascade impactor samples)
(b) Respirable mass loading, grams/cubic meter.
(c) High mass loadings and verified leak in baghouse.

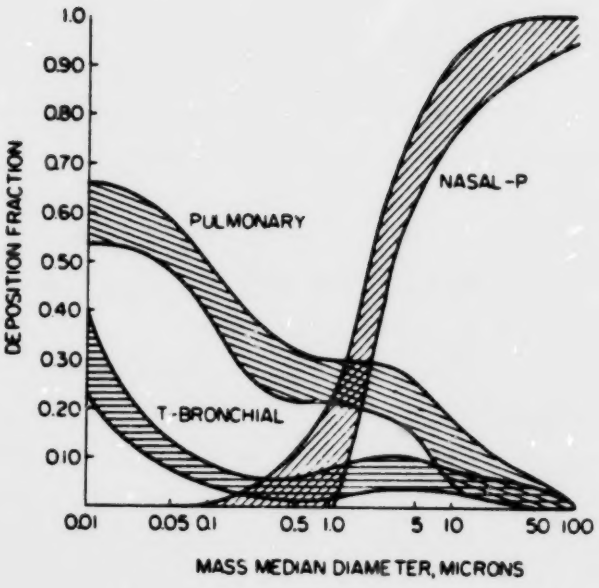


FIGURE 5 VARIABILITY OF DEPOSITION FOR A GIVEN MASS MEDIAN (AERODYNAMIC) DIAMETER IN EACH COMPARTMENT (8)

2.2.3 Data Gaps. To date, the size of AFBC residue particles has been determined by sieve and hydrometer techniques, techniques also used for soil testing. Based on weight distribution, the dry spent bed material of bubbling units initially has a particle size distribution like that of coarse sand, whereas the carryover particles appear to be clay-like in size. However, the low-cost sizing of particles below 100 mesh or about 0.1 mm presents significant difficulties. Hydrometer analysis has been used, but this type of testing is valid for particles that do not react with the liquid used in the procedure. Such is not the case for AFBC residues containing calcium oxide, which reacts with water. Thus, at best, hydrometer-based particle sizing can be used to provide approximate data on slaked or partially slaked residues. Where precise data are required, the results of such analyses must be interpreted with caution. Other, inexpensive testing methods are therefore needed to size particles in the 1-m to 0.1-mm range, because fine particles may contribute to the handling properties of the residues. It has been suggested that working liquids other than water, such as alcohol or kerosene, could be used with

hydrometry techniques. However, this has not yet been tried, and reactions affecting the particle size distribution might occur with these other fluids also. The use of liquids containing water or substances potentially capable of reacting with calcium oxide should be approached with caution, as rapid reactions and combustion may be possible.

Because most of the particles are of small diameter, the residues may generate considerable dust when handled. The dust factor may require special considerations in the design of equipment, such as in the seals, bearings, and lubrication systems, so that the equipment can be operated for an acceptable service life. In addition, fine particles often have been found to be difficult to wet. Suppression of dust by spraying water, either during transit or at the ultimate disposal site, would not likely be effective. Particles in this size range might also dry quickly, because of their large surface/mass ratio. These factors may lead to continuing fugitive dust emission at the disposal site, if steps are not taken to prevent it.

Results of limited sampling and analysis of very small particles indicate that sub-micron respirable particles are produced by AFBC and other combustion processes. This suggests that workers around the combustors, particularly at the waste material transfer points and at the disposal site, could be exposed to a respiratory hazard, if precautions are not taken. A detailed assessment of the potential hazards related to the fine particle size of AFBC wastes would require further sampling and specific occupational health-related data. Different analytical techniques would be necessary to determine particle sizes and concentrations, particularly for the size range below 1 mm.

2.3 Chemical Composition

A number of studies have examined the chemical composition of AFBC residues. The results of such testing may identify potentially hazardous properties, leachability, pollution and worker health problem potential.

2.3.1 General. The chemical composition of the wastes may be determined either on the solid material, using techniques such as x-ray analyses; or the residue can be dissolved and chemically analyzed, using techniques such as atomic adsorption or induced-coupled plasma spectroscopy. In Canadian studies, the unique properties of some AFBC residues necessitated development of an integrated analytical program encompassing wet chemistry, x-ray and spectroscopic methods. This situation arose partly because the wastes were of a new type and partly because of difficulties in quantifying the elemental and crystalline components in the wastes. This approach is described by Dearborn (5).

2.3.2 Relevant Data.

Bulk composition. For the initial Canadian studies, samples were obtained from the combustion of eastern Canadian high-sulphur coals in limestone at a bubbling-bed U.S. test facility. Residues were analyzed for elemental and crystalline composition. The bed materials were composed primarily of aluminum, calcium, iron, sodium, and silicon. The baghouse material contained relatively less calcium, but more iron and more sodium (5).

Given the knowledge of the combustion and sulphur capture processes, the large proportion of calcium in the waste suggests that much of the calcium might be present as calcium oxide. In significant amounts, this could pose a reactivity problem. Further testing was conducted in all subsequent studies to identify the principal crystalline calcium species present.

The high crystalline calcium oxide content indicated in the first studies was confirmed in subsequent studies. These identified the principal crystalline chemical constituents of residues from a series of bubbling AFBC pilot plant studies in which eastern Canadian high-sulphur coals and limestone were used (9). In a third study, calcium oxide was quantified in bed, cyclone and baghouse wastes (10). The calcium oxide content was greatest in the bed material and smallest in the baghouse material. Calcium sulphate showed a similar trend. Ferric oxide varied indirectly with the calcium content. The third investigation also determined the crystalline composition of bubbling AFBC residue samples taken from a wider variety of high-sulphur coal and limestone tests (10). (See Figure 6.) Again, calcium oxide was identified in the residue, with decreasing concentrations from the bed to cyclone to baghouse material.

Occupational health. The presence of crystalline calcium oxide in these residues could be significant in terms of the potential chemical reactivity of the waste. The reactivity raises possible concerns about environmental protection and the protection of human health. Farkas (11), for example, described the development of caustic ulcers when an agricultural worker was exposed to lime dust. The dust apparently got inside the top of the worker's rubber boots and onto his skin, where sweat dissolved the lime. Within 6 hours a burning erythema developed on his skin and within 24 hours a brown-black necrotic crust formed. During the healing process the dry crust was shed and scar tissue formed. This effect was attributed to the calcium oxide and calcium hydroxide content of the lime. Caustic chemical sensitivities have been described by others: Hannuksela *et al.* (12), Rycroft (13), and Vikers and Edwards (14). All attributed the sensitivities to skin contact with caustic cement or lime dusts.

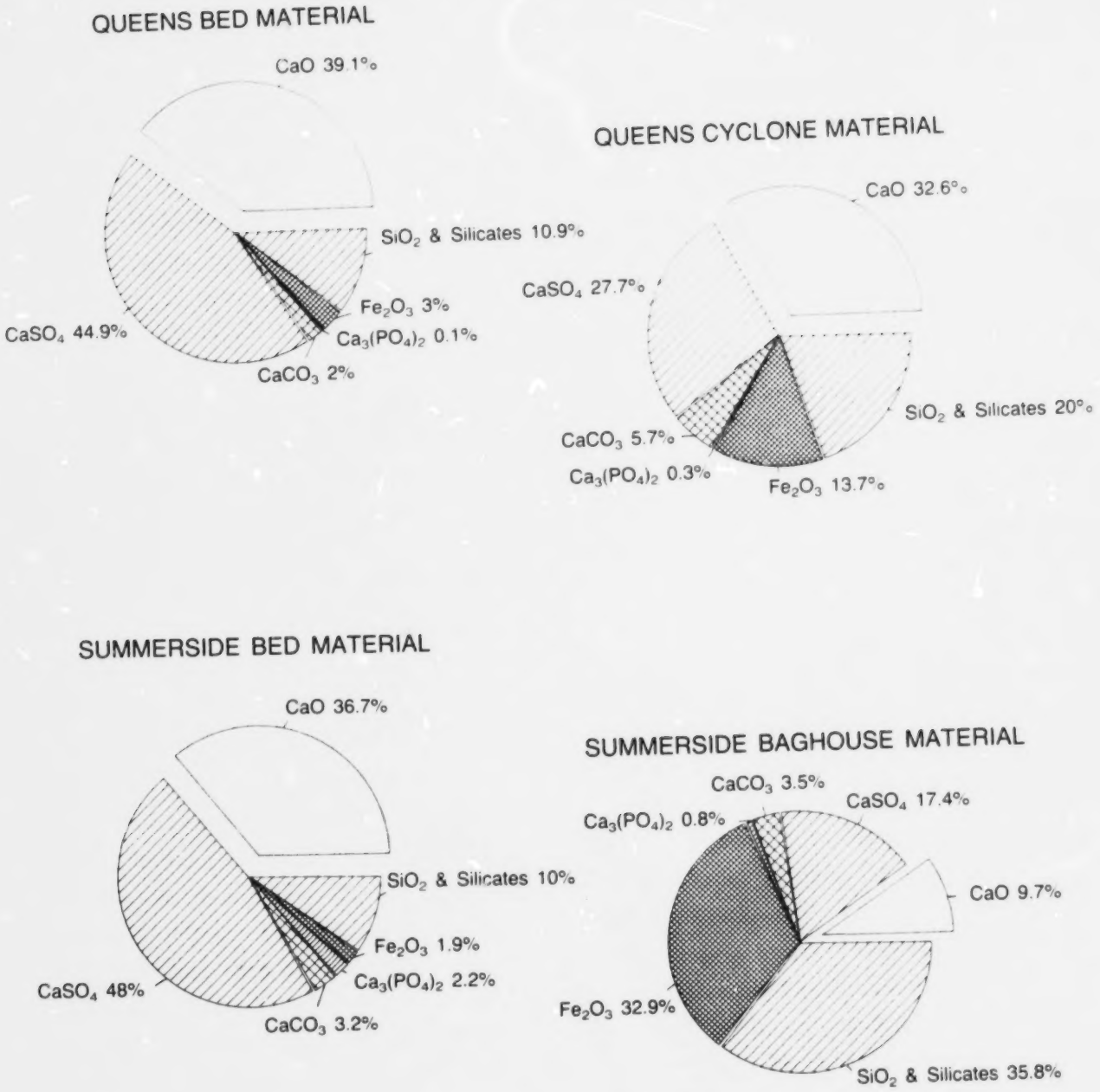


FIGURE 6 CRYSTALLINE COMPOSITION OF SELECTED RESIDUES FROM CANADIAN AFBC UNITS

Contact with caustic cement or lime dusts points to a potential health hazard for workers exposed to AFBC wastes containing calcium oxide not only to the skin but also, as mentioned earlier, to the respiratory tract.

NIOSH/OSHA have established health standards pertaining to workers exposed to calcium oxide (15). The permissible time-weighted average is 5 mg/m^3; 250 mg/m^3 is considered to be a concentration immediately dangerous to life or health. Concentrations of airborne calcium oxide could conceivably exceed the standard of 5mg/m^3, particularly at residue transfer points. Workers' exposure is more likely during handling of the residues or during maintenance operations. Target organs include the respiratory system, skin, and eyes. Inhalation may cause irritation of the upper respiratory tract, perforation of the nasal septum, or pneumonia. Contact with the skin can cause dermatitis or chemical burns. Contact with the eyes can cause chemical burns also.

Leachability. Chemical analyses of AFBC residues identified several readily soluble species. This suggests a large potential for environmental degradation in the event of uncontrolled disposal of the residues. Consequently, many studies have investigated waste leachability. The work of Grimshaw et al. (1) is one of the more exhaustive leaching studies which included both laboratory and field testing.

Several Canadian laboratory studies have also attempted to characterize leachates from Canadian coal/Canadian limestone AFBC residues.

In the first Canadian study (5) the residues investigated were spent bed material and baghouse material generated during a test burn at a pilot-scale AFBC unit. High-sulphur eastern Canadian bituminous coals were burned in a bed of eastern Canadian limestone.

Each residue was subjected to a multicycle serial batch leaching procedure (5). Two different liquid-to-solid ratios (4:1; 20:1) and two leaching media (deionized water at pH 5.5, and an "acidic" medium at pH 4.5) were used. The residues were radially agitated in closed containers. The settled leachates were filtered through 0.45-micron filter paper before analysis.

The leachates were highly alkaline, with pH values usually greater than 12, and contained high concentrations of dissolved solids. These were primarily calcium and sulphate ions, typically in concentrations greater than 1500 mg/L. Low concentrations of metals other than calcium, usually less than 1 mg/L, were also present in the leachates. This was not unexpected because of the high alkalinity of the leachates.

The second study (9) aimed at characterizing leachates from solid residues produced at two different bubbling AFBC installations. Both units used similar eastern

Canadian high-sulphur bituminous coals and eastern Canadian limestone under various operating conditions.

Residues were subjected to 20 serial batch leaching tests, using deionized water (pH 5.5) as the leaching medium, at a 20:1 liquid-to-solid ratio, for 25 hours in closed containers.

The resulting leachates were again highly alkaline with pH readings between 10.3 and 13.4. Total dissolved solid concentrations decreased from 4400 - 5500 mg/L in the first cycle to 120 - 1700 mg/L by the twentieth cycle. Major ion species in the leachates were calcium and sulphate. Minor constituents included chloride, sodium, potassium, fluoride, silicon, aluminum, and strontium; these elements were typically present in concentrations an order of magnitude lower than those for calcium and sulphate.

Chu et al. determined total organic carbon (TOC) in leachates from over thirty AFBC and PFBC wastes, covering various FBC processes and coals (16). The TOC concentrations were consistently less than 20 mg/L for all the leachates, except one baghouse leachate in which it was 30 mg/L. Simulated AFBC waste runoffs were found to contain small amounts of volatile and semivolatile organics. The levels of U.S. EPA priority pollutants occurred in concentrations typically less than 1 µg/L. However, phenol concentrations ranged up to 7.5 µg/L.

These low concentrations of organics may be due to the presence of unburned coal in the residues. Thus, the highest concentrations of organics might be expected in leachate from cyclone materials which contain unburned carbonaceous material. In general, however, organic compounds in AFBC residue leachates are not expected to cause serious environmental problems, particularly if combustion efficiencies continue to improve.

From the literature describing the chemical characteristics of AFBC waste leachates, it appears that the parameters of major concern are the high alkalinity and high TDS concentrations, mainly calcium and sulphate ions. Because of the alkalinity of the leachates, dissolved metals other than calcium were generally not found in significant concentrations. The concentrations of major ion species were greater in the bed material leachates than in the fly ash leachates, where the concentrations of trace elements and organics were usually greater.

The major chemical characteristics of the leachates were essentially the same for wastes from combustion in a limestone bed or in a dolomite bed. A comparison between leachates of AFBC fly ashes from combustion with and without a limestone

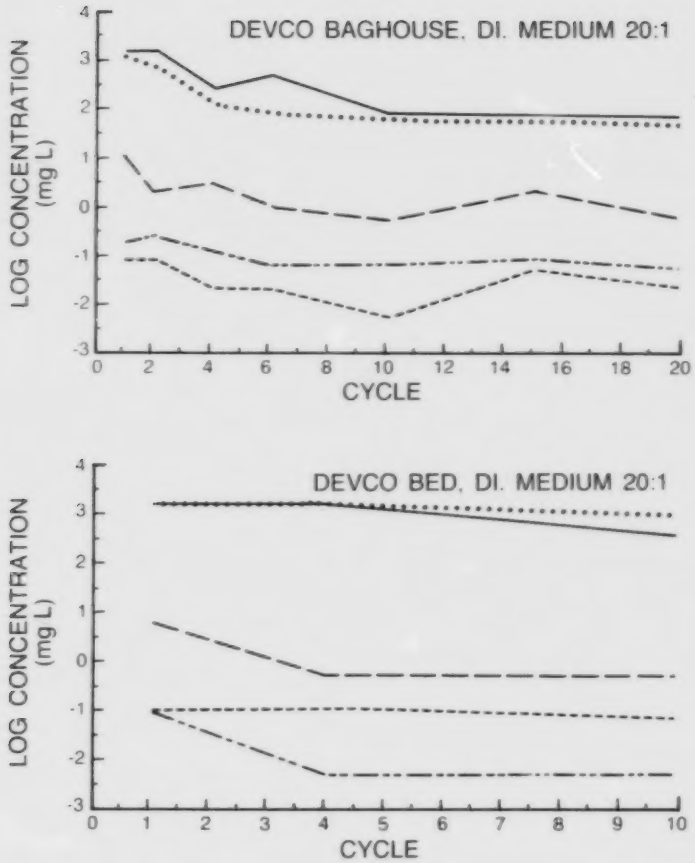


FIGURE 7 CONCENTRATION vs. CYCLE

sorbent indicates that sulphate and copper concentrations and the pH were greater where a sorbent was used during combustion; and boron, magnesium, manganese, and zinc were lower in the leachate from its waste.

Comparisons of laboratory and field leachates. Comparisons have also been made between laboratory and field lysimeter leachates of AFBC and PFBC wastes (1). The most significant difference between the laboratory (batch and column) and field leachates is the consistently more neutral pH of the field leachates. This appears to be due to either natural carbon dioxide uptake from the atmosphere or the breakdown of carbonates in the field lysimeters.

In addition to identifying and quantifying the chemical constituents of the AFBC wastes which can be leached, the long-term pattern of contaminant release is also important in assessing the potential problems of this type of residue.

Data from serial batch laboratory leaching tests are often used to estimate the long-term leaching potential of wastes under conditions similar to those of the test procedure. Figure 7 shows the leaching of sulphate, sodium, magnesium, iron, and calcium from AFBC waste, where deionized water is used as the leaching medium; gas interchange with the atmosphere has been excluded (5). The trend lines for concentration tend to be horizontal over the test period for both the baghouse material and bed material. This suggests a constant release of the species and an unlimited availability of the species under test conditions. For these chemical species the release rate does not decrease with time, and does not exhibit complex behaviour associated with solubility, pH, ionic strength, complexing effects, or changes in the surface of the residues particles.

Studies have also been conducted using large-diameter, disturbed-media lysimeters intended to simulate AFBC landfills. The field cells were thought to simulate full-scale disposal conditions more closely, where unsaturated flow, intermittent water inflow from natural rainfall, temperature fluctuations, and availability of atmospheric carbon dioxide could affect the release of chemical species from the wastes (1). (Figures 8 and 9 show the trends in concentration of calcium and sulphate over a 550-day test period.) Despite the simulated full-scale disposal conditions acting on the field cells, the concentrations of calcium and sulphate tended to be relatively constant. In this respect, these data tend to corroborate the laboratory data. The waste would continue to leach as long as water comes in contact with it. Hence, continuing groundwater contamination would result from improper or uncontrolled disposal of this type of residue.

A number of researchers investigating AFBC waste leaching, have suggested that, because of the high concentration of chemical species in the leachates and the

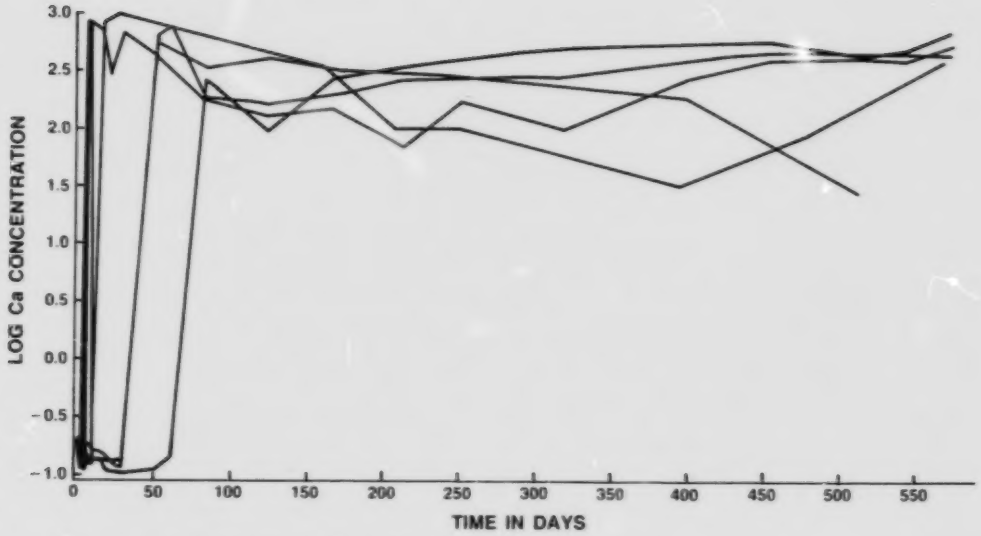


FIGURE 8 CALCIUM CONCENTRATION TRENDS (mg/L) FOR LEACHATES FROM THE UPPER SAMPLE POINT OF THE ALLIANCE AFBC FIELD CELLS

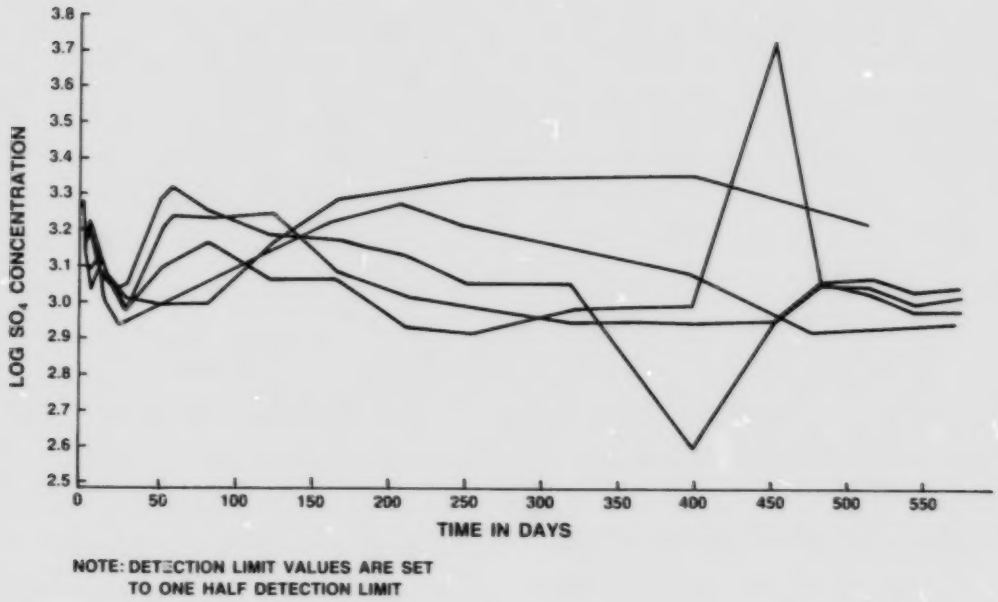


FIGURE 9 SULPHATE CONCENTRATION TRENDS (mg/L) FOR LEACHATES FROM THE UPPER SAMPLE POINT OF THE ALLIANCE AFBC FIELD CELLS

potential to generate these over very long periods, some form of leachate collection and treatment is necessary. Consequently, the treatability of leachates is an increasingly important area of investigation toward finding practicable and cost-effective methods of handling and treating wastewater.

Treatability study on leachates. A laboratory-scale physical/chemical treatability study was conducted using laboratory-produced leachates from AFBC residues (17). During the literature review preceding the study, no FBC-specific discharge criteria for the protection of the environment and no technical literature documenting the treatment of such leachates were found.

The treatability study investigated various treatment methods including sulphuric and hydrochloric acid addition, recarbonation, aeration, soda ash addition, and combinations of these methods. The performance of each method was rated in terms of its success in meeting the experimental discharge targets arbitrarily set for the evaluation. Acid addition methods met the pH targets; aeration and recarbonation methods met the pH and metal targets; and the combination of soda ash and sulphuric acid or recarbonation methods met the pH, metals and stringent calcium/hardness/alkalinity targets. The methods, other than hydrochloric acid addition, produced some sludge, typically less than 5 percent by volume. A TDS concentration target was not included but aeration and recarbonation treatments produced significantly lower TDS concentrations in treated effluents than acid addition alone.

Titration curves for acid addition and recarbonation treatments indicate that a significant portion of the reagent dose was used up in lowering the pH from 12.5 to 10.0, and a relatively minor fraction of the total dosage reduced the pH further to 7.0. Because the response of pH to additional reagent is very sensitive between pH 10.0 and 7.0, the reaction would have to be very closely controlled to prevent overshooting the target pH range. An acidic medium resulted in a TDS increase. Similarly, for aeration, only a small percentage of the total air dosage was required to reduce the pH from 10.0 to 7.9. Additional aeration did not reduce the pH further, so over-acidification is not a problem with aeration. Again, the aeration treatment results indicate that the previously noted discrepancies between the pH values for field- and laboratory-produced leachates were probably caused by differences in carbon dioxide absorption. This also suggests that previous studies on laboratory leachates may not have permitted sufficient time or air contact for natural carbonation to occur.

The untreated AFBC leachates had an extremely high scaling potential as measured by the Langelier Index. In the laboratory tests, some of the treatment methods

reduced the scaling tendency. However, most of the treated effluents still retained a slight to moderate tendency to scale. This characteristic might seriously affect operation of a wastewater treatment plant and limit the recirculation options in wastewater management system designs.

The material costs for the treatment of 1 m^3 of wastewater ranged from $0.37 for aeration to $8.32 (1985) for recarbonation. These costs include neither capital costs nor the costs for construction, labour, and maintenance. When these additional factors are taken into account in different size classes, overall costs for each treatment would vary considerably.

2.3.3 Data Gaps. Through chemical characterization studies the principal crystalline species present in AFBC residues have been identified. Among these is a high proportion of calcium oxide, particularly in the bed material, which results in a reactive waste with some potentially hazardous properties (see 2.4). The studies of residues so far have been from pilot- or demonstration-scale bubbling units burning high-sulphur coal in a limestone bed at calcium-to-sulphur ratios of about 3:1. It has not yet been demonstrated that new, large-scale combustors will continue to produce wastes with similar properties. The newer circulating-bed designs are expected to produce wastes with somewhat different characteristics as well. Presumably, as the control technology improves it may be possible to operate combustors with the same sulphur capture but with improved calcium utilization. This will reduce the amount of calcium oxide in the residues and thus reduce the reactivity and alkalinity, and hence, the potential hazards of such wastes.

Leaching protocols. The leaching protocols used to date have tended to produce "worst case" leachates because of the high liquid-to-solid ratio and long contact time. Most protocols are also conducted in sealed containers, preventing the uptake of carbon dioxide from the atmosphere by the wastewater. This appears to result in laboratory-produced leachate with contaminant concentrations greater than those that would occur in field situations. Some field lysimeter studies have resulted in nearly neutral leachates, in contrast to the highly alkaline leachates produced in the laboratory. These field results correspond to the results of experimental aeration and recarbonation treatments of leachates. Consequently, it is still unclear how well the laboratory leaching protocols used to date actually simulate all, or even most, in-field physical and chemical situations which are likely to be encountered.

Large-scale handling and disposal methods. It appears that generally the unprocessed AFBC residues from the bubbling units examined to date are, because of their

calcium oxide content and solubility, environmentally unacceptable for direct, uncontrolled land disposal. Environmental concerns centre mainly on pH, calcium, sulphate, and TDS in potential leachates. The leaching problems related to this waste may be temporary, if aeration occurs. Under certain conditions, it appears they can persist for a very long time, as long, in fact, as water is allowed to percolate through the waste.

Large-scale handling and disposal methods for FBC wastes of this type are as yet virtually nonexistent. Such techniques need to be developed. To develop them properly, though, more information about waste reactions is required. At the moment, an important aspect of disposal area design would appear to be the minimization of water contact with the wastes to reduce the volumes of leachate which might form, and subsequently the runoff that needs to be captured and treated.

The concentrations of most trace elements in the leachate are low, primarily due to the alkalinity of the wastewater. Treatment methods for wastewaters of this sort would likely be quite different from those developed for wastewaters from other high-sulphur coal combustion processes. Thus, new characterization procedures and the establishment of standards, which acknowledge these differences, may be necessary.

Conditioning of residues. It might also be possible to process or condition AFBC residues prior to disposal to reduce their reactivity or make them more stable in contact with air and water. Treatments such as dead burning, slaking, or slurry carbonation might reduce the reactive properties and leachability of these wastes. However, pretreatment has not yet been studied in depth and requires further investigation.

Basic treatments of laboratory-produced AFBC leachates has been demonstrated; however, they need further refinement. The chemical requirements, costs, and process configurations need to be extended from laboratory to pilot scale, so that the costs of treatment can be determined with confidence. This type of data is also required to optimize alternative disposal area designs and evaluate them for cost effectiveness.

2.4 Chemical Reactivity

Both the bubbling-bed carryover, or fly ash, and the spent-bed material from combustion in a limestone bed may contain large proportions of crystalline calcium oxide. In addition to affecting the properties of their dusts and the leachability of the residues, the reactions of calcium oxide with water and air may also affect the chemical reactions of the rest of the waste mixture. The extent and rate of the chemical reactions in the

waste mixture appear to depend mainly on the amount and reactions of calcium oxide in the combustion residues.

2.4.1 Relevant Data

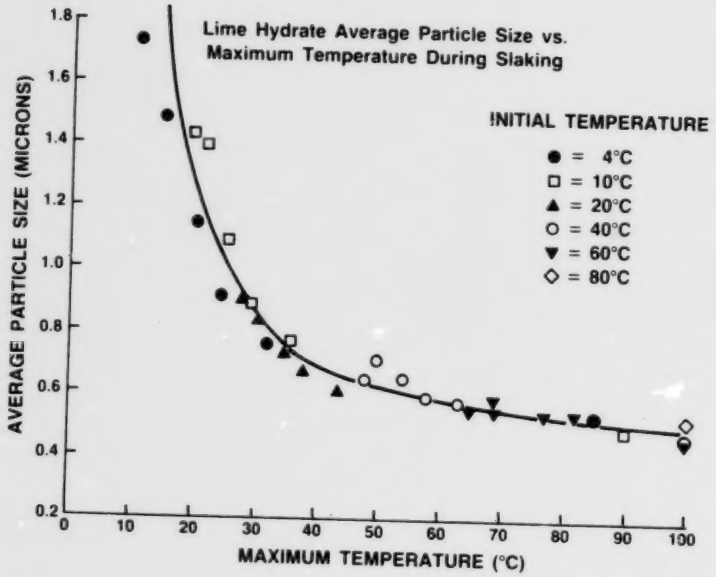
The lime-water reaction. The reaction between calcium oxide and water is known as hydration or slaking. The reversible chemical reaction for the slaking of calcium oxide is as follows:

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 + Heat$$

This reaction is strongly exothermic; that is, heat is liberated during the chemical reaction at 1.14 MJ/kg of calcium oxide. Boynton (18), for example, noted that this pronounced heat release, characteristic of lime, has caused leaky wooden box-cars carrying bulk quicklime to ignite and burn as a result of the cargo becoming wet during rainstorms.

When calcium oxide is brought into contact with water, the reaction is virtually instantaneous. The reactivity with water and rate of heat release are, however, largely determined by the rate of water penetration into the mass, which, in turn, depends on the pore structure and surface area of the quicklime particles. Pore structure and surface area are factors that, in effect, limit the contact area. The rate of reaction with water generally increases with increasing surface area, as shown in Figure 10 (19). Figure 10 also shows that a greater maximum temperature can be expected with smaller particles. The reaction forming calcium hydroxide is accompanied by an increase in material volume because of increased solid mass, reduced solid density, and increased temperature. During the slaking reaction, the volume increase of the crystals causes the quicklime particles to disintegrate into microscopic particles. As the reaction proceeds, the evolved heat raises the temperature of the slaking water and the reaction is further accelerated (20). The assimilated water is chemically combined to form calcium hydroxide. No hydrates have been unequivocally identified. This contrasts with other chemicals, such as sodium sulphate decahydrate ($Na_2SO_4 \cdot 10H_2O$), in which the water is present as a hydrate. For the complete hydration of pure calcium oxide, 0.32 kg of water/kg of calcium oxide is required. The hydration of 100 kg of quicklime forms 132 kg of calcium hydroxide.

Glasson (20) determined that the surface areas of various calcium oxide samples differs widely (specific surface of 1 to 100 m^2g^{-1}) as did their surface activity when exposed to water vapour at room temperature. Although the rates of hydration



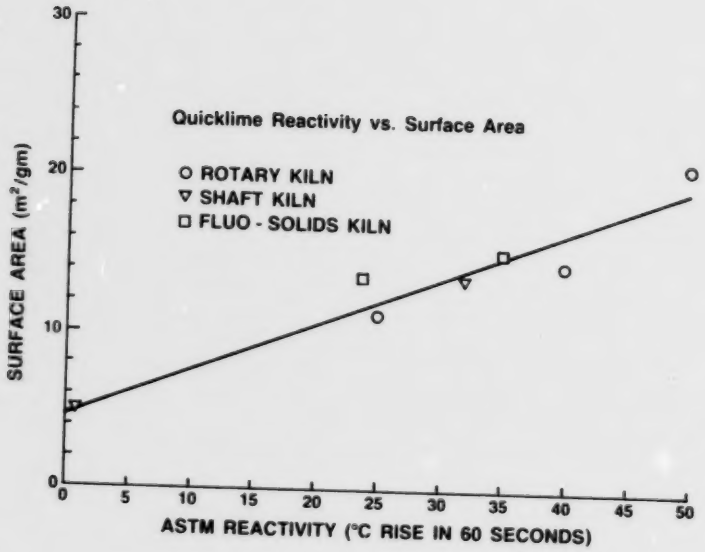


FIGURE 10 REACTIVITY OF QUICKLIME vs. SURFACE AREA AND RELATIONSHIP BETWEEN PARTICLE SIZE AND MAXIMUM TEMPERATURE

differed considerably, each sample took up in chemical combination a stoichiometric quantity of water. It was found by studying changes in surface area and crystal lattice structure during hydration that active limes agglomerated rapidly in the presence of water vapour and had to be hydrated at very low relative pressures to maintain the same number of crystallites. Limes of moderate activity could be hydrated without agglomerating. Least reactive limes underwent hydration only when the number of crystallites increased; the necessary fission of the original crystallites was accompanied by slow rates of hydration. The hydration reaction was found to proceed from the outside of each calcium oxide particle by an inwardly advancing interface mechanism.

Quantitatively, during hydration the number of crystallites decreases. Each CaO-crystallite should form a $Ca(OH)_2$-crystallite having 1.98 times the volume at 1.54 times the surface area. However, the overall change in surface area was less than this, indicating that loss of surface area due to agglomeration occurred (20).

Although some insight into the reactivity of AFBC combustion wastes can be gained from examining the theory of lime slaking, Boynton (18) has pointed out that the optimum hydration rate and conditions must be empirically and individually established for individual lime sources. To this end, several techniques, applicable to AFBC materials, have been developed to quantify the activity of quicklime-containing materials. These can be broadly classified as either calorimetric or static column procedures.

Calorimetry. This approach to quantifying the heat release from a slaking reaction involves adding a known amount of sample to a known amount of liquid, stirring, and recording the temperature rise at intervals over the reaction period.

Calorimetric Test Procedures. ASTM C110-76 (21) provides a test protocol in which 76 g of quicklime is added to 380 mL of distilled water (liquid-to-solid ratio of 5:1) in a modified Dewar flask covered with a rubber gasket and fitted with a mechanical stirrer.

The temperature is observed on a thermometer at 30- to 300-s intervals, depending on the reactivity of the quicklime, until a constant temperature has been reached.

The American Water Works Association has a similar standard procedure (22). In this protocol 100 g of lime is added to 400 mL of water. Thus a 4:1 liquid-to-solid ratio is used. The temperature increases are correspondingly higher.

Murray (23) studied the reactivity of lime as a function of porosity and shrinkage characteristics during calcination and found that calcitic quicklimes of low shrinkage and high porosity are highly reactive. The procedure used an empirically

selected liquid-to-solid ratio of 7:1 by weight. The procedure was used to evaluate extremely reactive limes in which slaking was completed in 3 to 4 seconds.

Reactivity of Calcium Oxide	Time to Reach 40°C (min)	Time for Reaction to Complete (min)
High	<3	<10
Medium	3-6	10-20
Low	>6	>20

Dearborn (5) conducted thermal reactivity tests on AFBC residue based on the ASTM procedure for lime at liquid-to-solid ratios beginning at 10:1 and decreasing to 5:1 and 3:1. This was believed to be the most cautious approach to quantifying the chemical reactivity of a material for which no prior data existed.

A liquid-to-solid ratio of about 6.7:1 was found to give the best repeatability (24). A lower liquid-to-solid ratio would give a greater temperature rise but would lack reproducibility, most likely due to local temperature variation. A higher ratio gave smaller exothermic effects, although it could, in some cases, provide greater sensitivity.

The procedure developed by Dearborn (5) for ash from bubbling FBC also differed from the ASTM procedure for lime with respect to the time over which temperature was observed. The reaction of water and AFBC wastes required a considerably longer time to achieve maximum heat release than with pure calcium oxide. Temperatures were monitored for up to 3 hours, whereas standard lime testing rarely exceeds 30 minutes.

Calorimetric Test Results. Researchers in the U.S. have investigated the exothermic properties of AFBC wastes through heat release tests on spent bed and carryover/fly ash materials from several bubbling AFBC units (25). Temperature rises in an AFBC spent bed material and in calcined limestone at various liquid-to-solid ratios are shown in Figure 11. Figure 12 shows temperature rises in several AFBC wastes at a liquid-to-solid ratio of 0.25:1. Higher temperature rises and faster responses were observed at lower liquid-to-solid ratios. The maximum temperature rise observed in the spent bed material at the lowest liquid-to-solid ratio was approximately 75°C. These data, shown in Figure 12, also point out the variation in heat release between various

AFBC residues. For spent bed materials, the temperature rise at 7 minutes varied between 4° and 75°C. The time taken to reach maximum temperature varied between about 1 and 12 minutes depending on the residue.

Unfortunately, not all studies reported the form of the calcium in the material tested or gave complete information about the test conditions, such as rate and method of water addition and the elapsed time at which the maximum temperature of the reaction was obtained. Consequently, direct comparisons between results are difficult and often appear contradictory. For example, Stone and Kahle (4) reported maximum temperature increases of about 90°C and 210°C in two spent bed materials and maximum increases of 1° and 13°C in two fly ash samples. These differences may have been accounted for by calcium oxide contents, had they been reported.

Temperature rise and heat release from bubbling AFBC residues from a U.S. test unit, the Queen's University pilot plant, and CFB Summerside heating plant have also been determined by calorimetry. A variety of eastern Canadian high-sulphur bituminous coals were combusted with Havelock limestone in these units. Table 2 summarizes the results of this testing. For Queen's residues, both the bed and cyclone materials 301.2 kJ/kg (72 kcal/kg) had average heat releases about six times greater than those from the baghouse material 51.5 kJ/kg (12.3 kcal/kg). In contrast, for Summerside the baghouse heat release 265.3 kJ/kg (63.4 kcal/kg) was greater than that from the spent bed material 224.7 kJ/kg (53.7 kcal/kg). In these tests the residues were near room temperature when the slaking reaction was initiated. However, in the field the waste temperatures may be several hundred degrees Celsius above ambient when the reaction is started, or when water at greater than ambient temperatures is used to slake the waste. The reaction under these conditions has not been investigated yet, but is expected to be much faster than that shown in Figure 11.

Figure 13 shows the temperature rise for two spent bed materials at four liquid-to-solid ratios. Temperature increases are inversely related to liquid-to-solid ratio. The rate of increase was faster at the higher liquid-to-solid ratios. Both bed materials showed slightly greater temperature increases on testing with the acidic medium (pH 4.5) than with deionized water (pH 5.5), particularly at higher liquid-to-solid ratios.

The results also indicate that, although the exothermic reactions were largely complete after 30 minutes, temperatures continued to increase past this time, particularly at the liquid-to-solid ratio of 1:1.

Similar calorimeter tests were also conducted on different particle size fractions of the two bed materials, using deionized water and the acidic medium at a

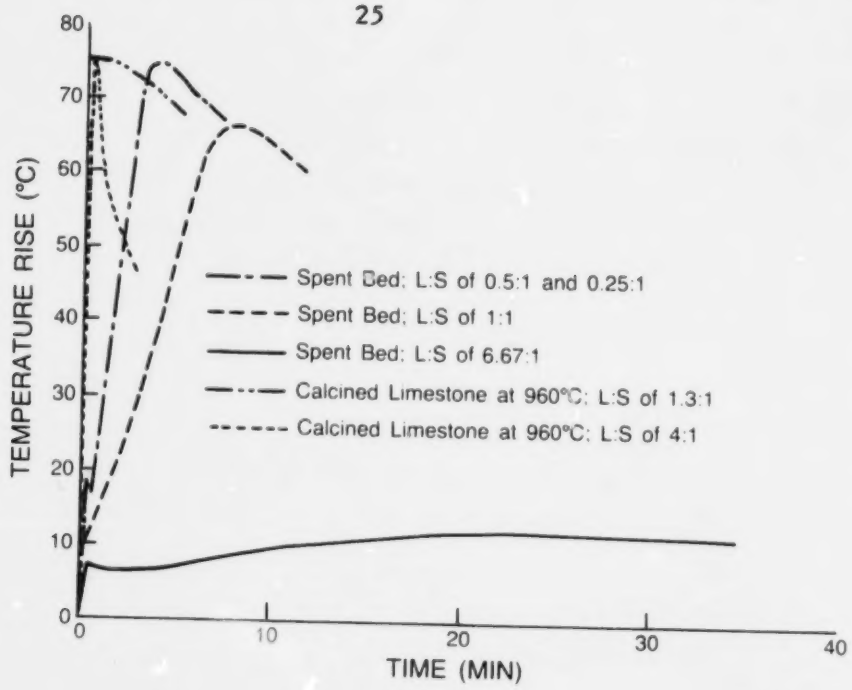

TEMPERATURE RISE (°C)
TIME (MIN)
Spent Bed; L:S of 0.5:1 and 0.25:1
Spent Bed; L:S of 1:1
Spent Bed; L:S of 6.67:1
Calcined Limestone at 960°C; L:S of 1.3:1
Calcined Limestone at 960°C; L:S of 4:1

FIGURE 11 HEAT RELEASE OF AFBC SPENT BED MATERIAL AND CALCINED LIMESTONE AT DIFFERENT LIQUID-TO-SOLID (1:5) RATIOS

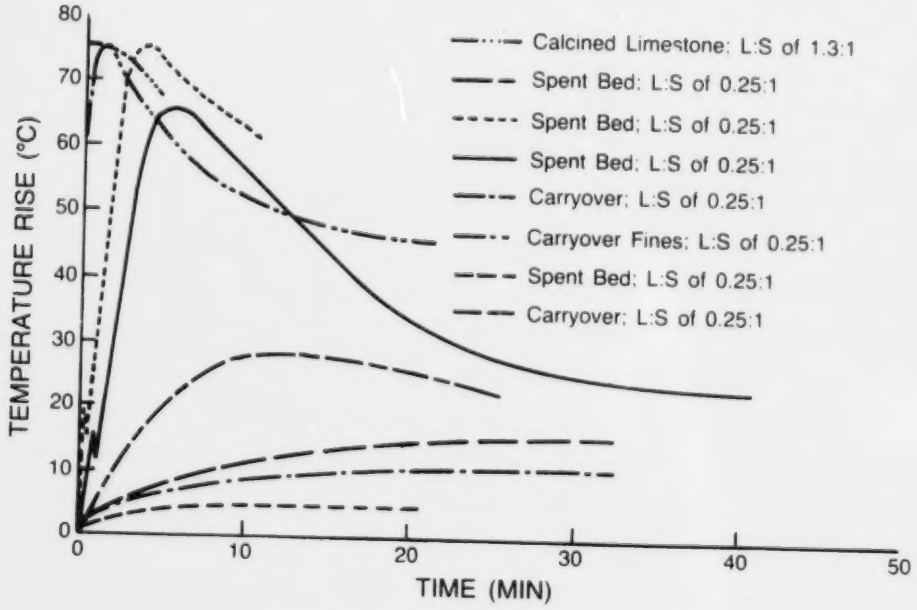

TEMPERATURE RISE (°C)
TIME (MIN)
Calcined Limestone; L:S of 1.3:1
Spent Bed; L:S of 0.25:1
Spent Bed; L:S of 0.25:1
Spent Bed; L:S of 0.25:1
Carryover; L:S of 0.25:1
Carryover Fines; L:S of 0.25:1
Spent Bed; L:S of 0.25:1
Carryover; L:S of 0.25:1

FIGURE 12 HEAT RELEASE OF AFBC SPENT BED MATERIAL AND CARRYOVER AT A 0.25:1 LIQUID-TO-SOLID RATIO

liquid-to-solid ratio of 1:1. Tests could only be conducted on the materials retained on the No. 20 and 40 sieve sizes and that passing the No. 40 sieve. The material captured on the No. 10 sieve was too large to be used in the test apparatus.

TABLE 2 HEATS OF REACTION OF AFBC RESIDUES

			Heats from Material (−ΔH; kcal/kg)		
Combustor	Coal	Limestone	Bed	Cyclone	Baghouse
U.S. Test Unit	Minto and Wood chips	Havelock	124	--	--
	Devco		38	--	14
Queen's	Evans	Havelock	42.8 ± 4.6*	112.1 ± 3.5	16.3 ± 5.7
			31.7 ± 8.0	57.3 ± 0.7	6.1 ± 0.6
			27.5 ± 1.7	83.7 ± 1.5	10.4 ± 1.7
			102.1 ± 10.8	84.1 ± 3.4	8.9 ± 2.3
			99.8 ± 5.3	88.6 ± 3.4	19.0 ± 3.3
			100.2 ± 7.7	27.7 ± 5.7	12.9 ± 3.7
	MEAN		70.8	75.6	12.5
Summerside		Havelock	53.7 ± 2.9	-	63.4 ± 1.3

* ± one standard deviation

Temperature variations in the three particle size fractions are shown in Figure 14. For the Devco bed material fractions, the most rapid and greatest temperature increase was observed with the material captured on the No. 20 sieve, followed by that on the No. 40 sieve and the pan material. The acidic medium produced a more rapid rate of temperature rise and, in the case of the pan material, a slightly greater temperature increase. Temperature increases during the first 20 minutes were the same for all three Devco bed fractions.

In the tests on the Minto bed fractions, for the first 60 minutes the sieve No. 20 material gave the greatest temperature rise followed by the No. 40 sieve and smaller materials. However, after 60 minutes, the greatest temperature rise was observed in the material on the No. 40 sieve.

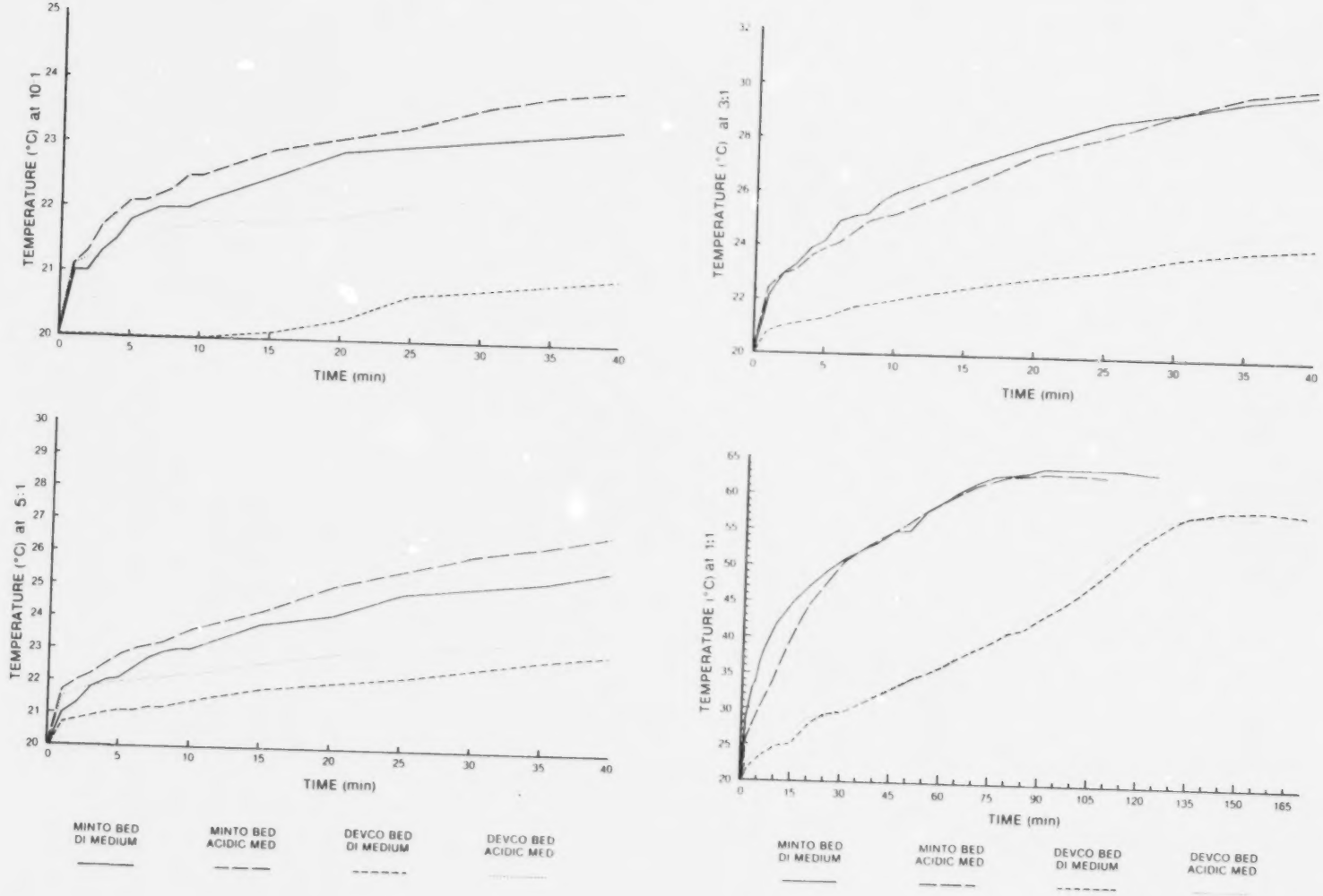


FIGURE 13 TEMPERATURE INCREASES IN THE MINTO AND DEVCO BED MATERIALS AT FOUR DIFFERENT LIQUID-TO-SOLID RATIOS

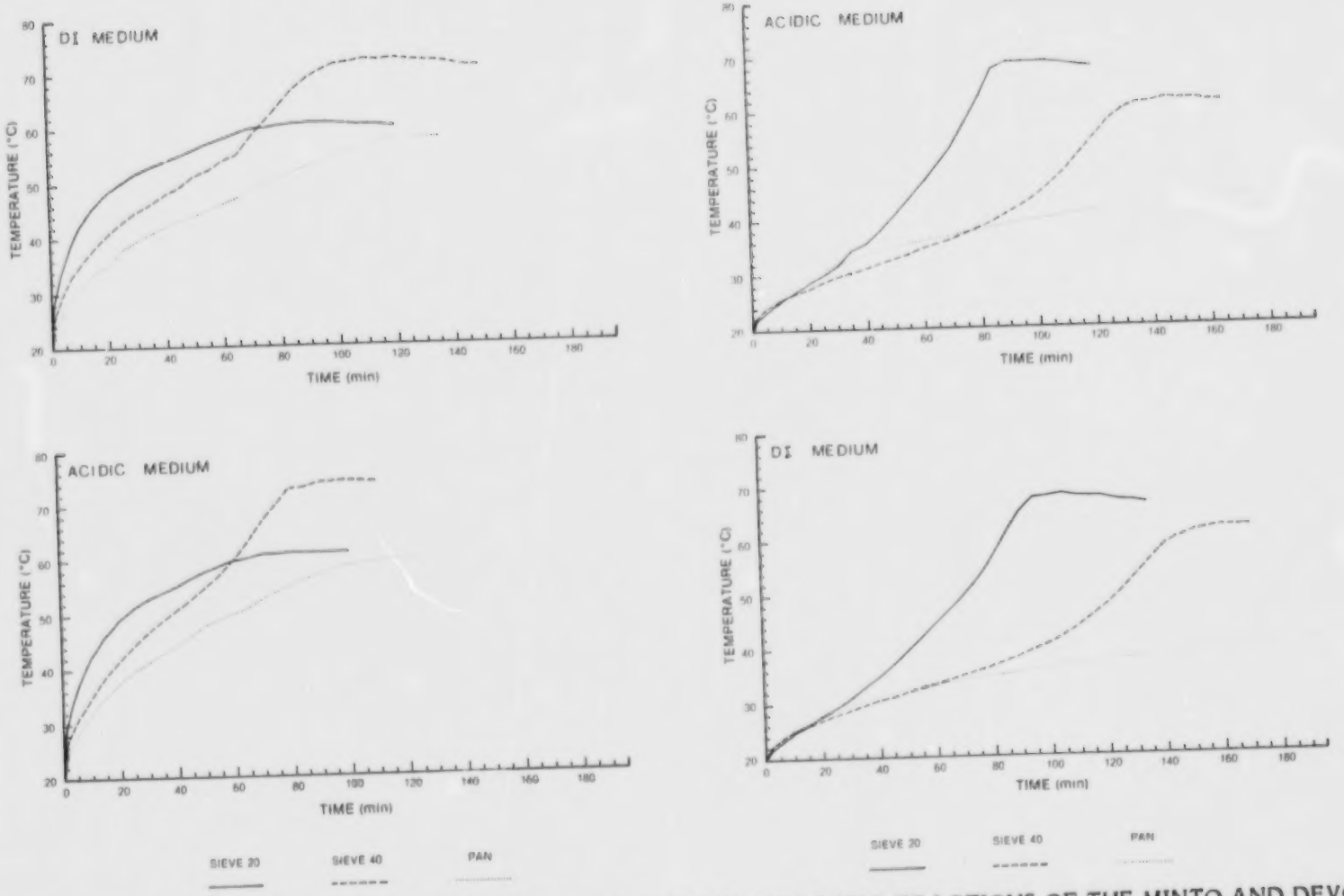


FIGURE 14 TEMPERATURE VARIATIONS IN THREE PARTICLE SIZE FRACTIONS OF THE MINTO AND DEVCO BED MATERIALS

Unlike the Devco bed fractions, differences in temperature increases in the Minto fractions were distinguishable from the start of the tests. The acidic medium produced both a slightly greater temperature rise and rate of temperature rise than did the deionized water.

In these tests the amount and rate of heat release were expected to be influenced not only by the residue composition and liquid-to-solid ratio, but also by particle size: the smaller the particles, the more reactive they should be. The heat of reaction of the bed and cyclone material correlates with the calcium content and buffering capacity. For baghouse material, no correlation exists with the calcium or sulphur content or buffering capacity. Buffering capacity was included in this analysis since the test procedure essentially measures all free alkali material in the sample and it was thought that the free alkali material is primarily calcium oxide.

Column testing. A static column test was developed by Dearborn (5) to quantify the time/temperature relationships of AFBC residues. The objective of this test is to examine the exothermic reactions using larger masses in a configuration approaching a field situation.

Column Test Procedure. Since no standard procedure existed, a developmental program was conducted, consisting of several successive test configurations. The first test column used was a polyvinyl chloride (PVC) pipe (2.54-cm I.D). It deformed and failed in the course of a violent reaction and was replaced by an insulated Schedule 40 PVC pipe (8-cm I.D., 40 cm high). However, this column also deformed and failed during the initial test series. The exothermic reactions increased the column temperatures to above 100°C. This caused the column shapes to distort and melt the insulation applied to one of the columns.

The third column design did not fail in the initial tests and was subsequently used. It consisted of a stainless steel tube (8-cm I.D., 40 cm high) lined with a teflon sleeve and fitted with five dial thermometers (replaced by sturdier thermocouples for later tests). Thermometer 1 was located about 4 cm below the surface of the material in the column. Thermometers 2 to 5 were positioned at 4-cm intervals vertically down the column. The column was covered with fiberglass insulation and held vertically in a retort stand. Deionized water was added to the top of the column at a rate of 1.24 mL/min (equivalent to a precipitation rate of 1.6 cm/h). The top of the column was filled with a layer of glass beads to help distribute the flow evenly over the surface of the material. Temperatures at the five positions were recorded at 5-min intervals. Monitoring

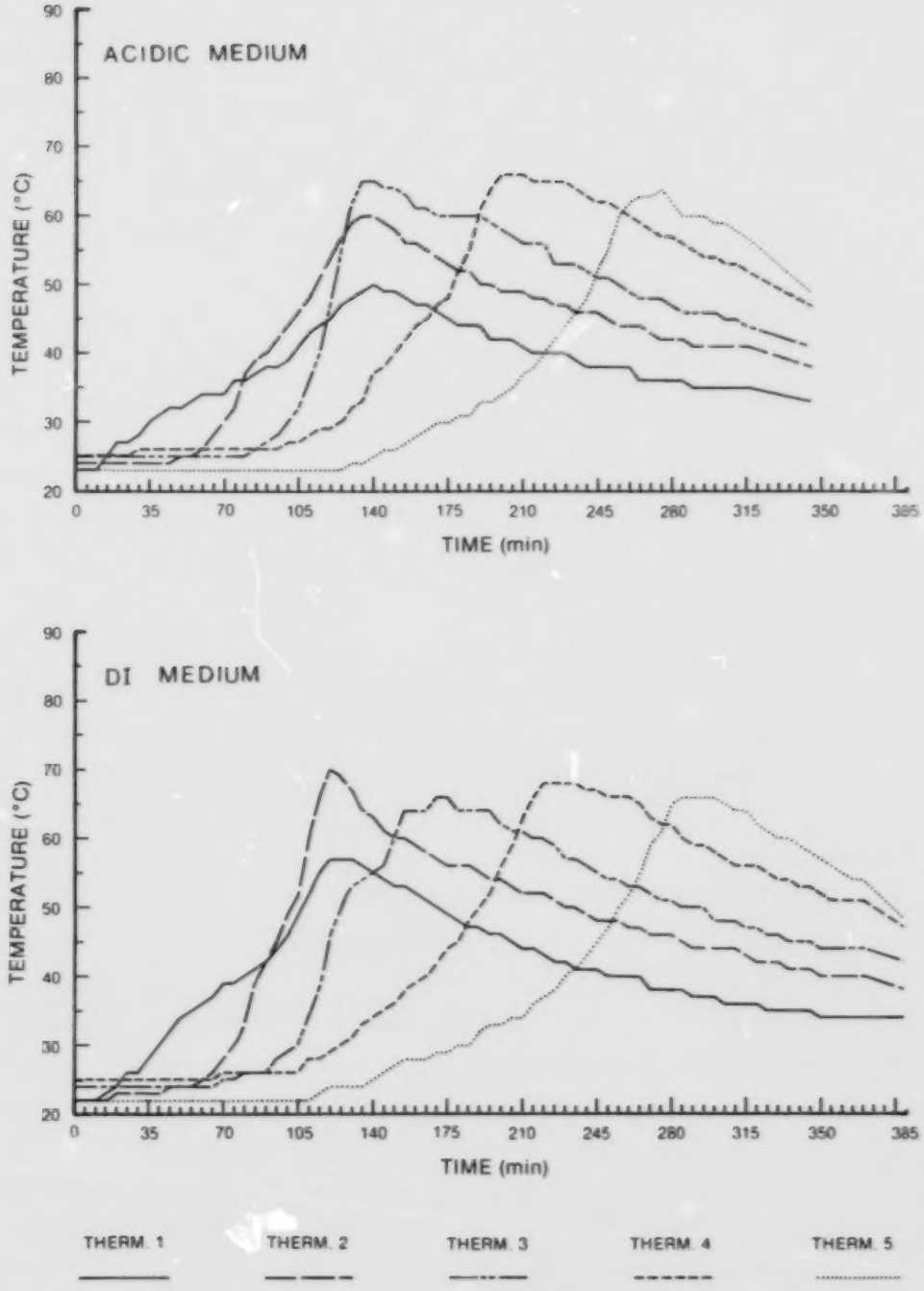


FIGURE 15 TEMPERATURE VARIATIONS DURING THE EXOTHERMIC COLUMN TESTS

continued until approximately 45 minutes after the bottom thermometer registered a peak.

Column test results. Figure 15 shows the results of the exothermic testing for two bed materials using two different liquids in the 40-cm steel column.

A time lag was evident before the increase in temperature at each thermometer. The lag increased with depth. The rate of temperature rise was greatest for the top thermometer and decreased with depth. The highest temperature occurred at a depth of about 15 cm.

The maximum temperatures indicated by the five thermometers were reached sequentially from top to bottom of the column at approximately 50-min intervals. This indicates that the water travelled through the material at a relatively uniform rate. In general, the overall shape of the temperature-versus-time plot for each thermometer, regardless of position or liquid added, was quite similar.

In these tests the heat releases observed with the steel column apparatus were similar to those observed with the ASTM calorimeter procedure. Temperature rises were of the order of 60°C and depended on both the liquid and the spent bed material used. During exothermic testing in the column, expansion of the bed material was observed. This is consistent with the particle expansion phenomenon associated with lime slaking.

High temperatures were also observed in subsequent testing with the steel column. Figure 16 shows the temperature increase with time for a bed material from the Queen's pilot plant. As indicated, a temperature rise above 150°C was recorded and, unlike the earlier results, the residues, when reacted, developed significant strength properties similar to those of concrete. Such strength development and temperature rises have since been demonstrated by other testing as well.

The results of this column testing indicate that this residue may have unique properties affecting its management but which are not necessarily apparent from the other characterization test procedures conducted on a smaller scale. The larger column tests resulted in some temperatures higher than those from earlier bench-scale calorimetry determinations. This demonstrates that there is a mass-related effect and that higher temperatures are possible when larger masses are slaked.

The column testing demonstrates that temperatures greater than 100°C are possible. Once temperatures greater than 100°C occur, another set of waste management design problems, such as liner material integrity and design requirements, must be considered for proper disposal of this type of wastes.

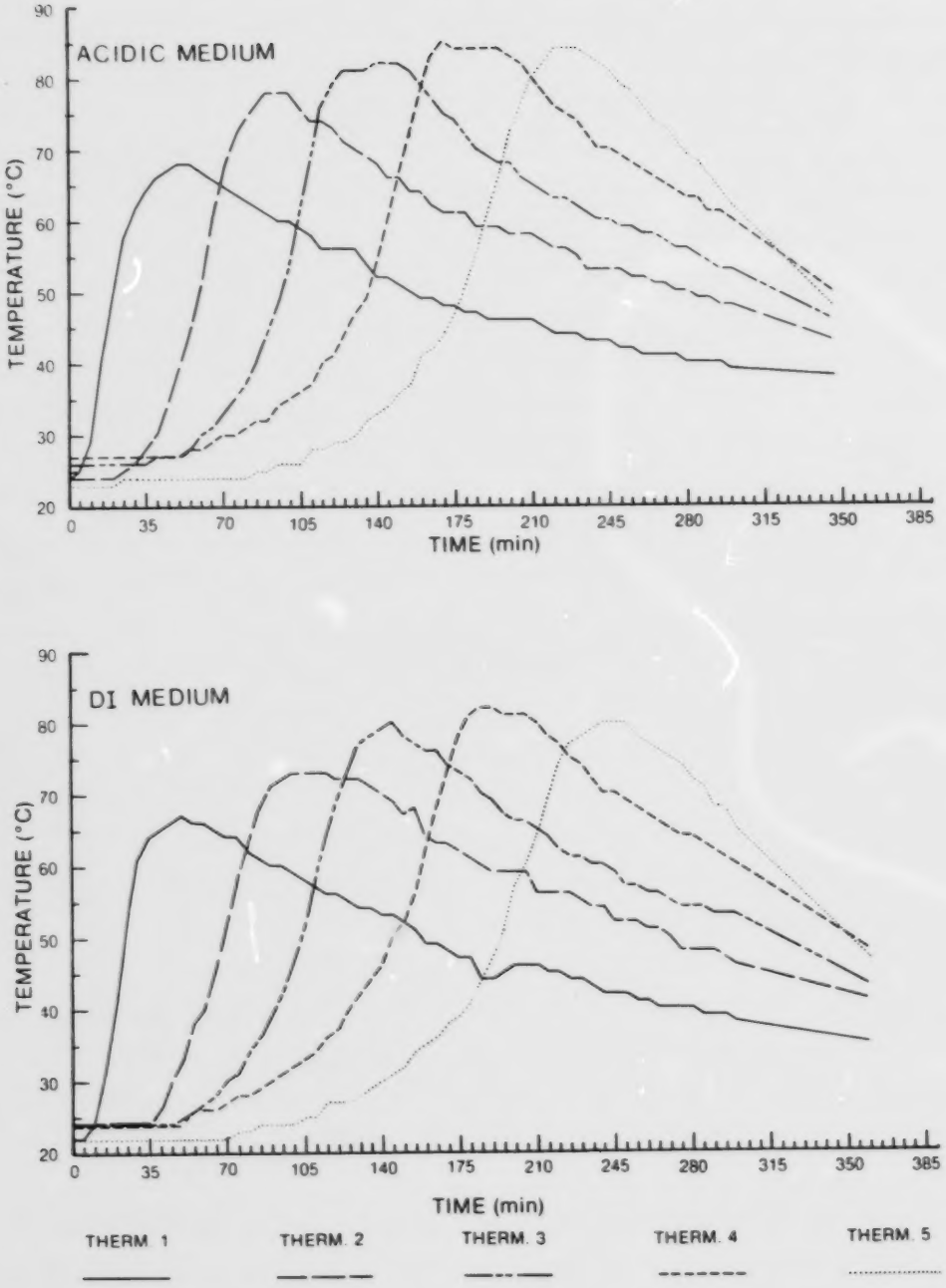


FIGURE 16 TEMPERATURE RISE USING COLUMN SLAKING APPARATUS

Finally, the variability or change in properties of the residues with time is not known. In some cases, large heat releases occurred which were not subsequently observed for the same waste sample. This indicates that the residues can behave in an unpredictable manner. Therefore, designs would need wide factors of safety to ensure that the conditions that might lead to unpredictable behaviour are avoided.

Effects of ions on slaking. In technical literature on the slaking of lime it has been suggested that the dissolved solids in the water could significantly affect the lime slaking process. Knibbs and Gee (cited in (27)) list several substances, including chlorides, that are known to accelerate the slaking of lime, and several others that retard the reaction. They also note that sulphates change the nature of hydration. Boynton (18) pointed out that variables in the slaking process can influence the mechanism by which hydrate crystals are formed. Baker and Jordan (27) studied the slaking reaction by using water with high TDS from a FGD scrubber and, for comparison, tap water. Presumably the scrubber water was saturated with calcium, sulphate, and other waste ions (TDS of 52 000 mg/L), whereas the tap water had a TDS of 55 mg/L. The slaking reaction at two liquid-to-solid ratios, the liquid being distilled water, was also evaluated. The temperature rise with time for these are shown in Figures 17 and 18. When slaked with tap water, the temperature reached 100°C, and the reaction was completed within 2 minutes. Figure 19 shows the rate of slaking using a variety of slaking water qualities.

The effects of using water containing 10 000 mg/L of sulphates as salts of calcium, magnesium, and sodium were studied. The retarding effect of sulphates is apparent (Figure 20). No major difference in effect is attributable to the accompanying cations. Figure 21 shows the effect on slaking rate of 10 000 mg/L of chloride added as salts of calcium, magnesium, and sodium. Chlorides accelerate the slaking rate. Finally, Figure 22 shows the effect of 10 000 mg/L of sulphur as sodium sulphate, sulphite, and bisulphite on the slaking reaction.

The results clearly indicate the accelerating effect of chlorides and the retarding effect of other anions containing sulphur such as sulphites, sulphates, and bisulphates. Retardation is demonstrated by reduced slaking temperatures and the increased time required for slaking to be completed. These data indicate that the rate of heat release from the slaking of AFBC residues can be reduced by using water containing selected ions for the reaction. This has special implications when waters of lower quality, such as wastewaters, are considered for slaking as a means of reducing total in-plant wastewater volumes.

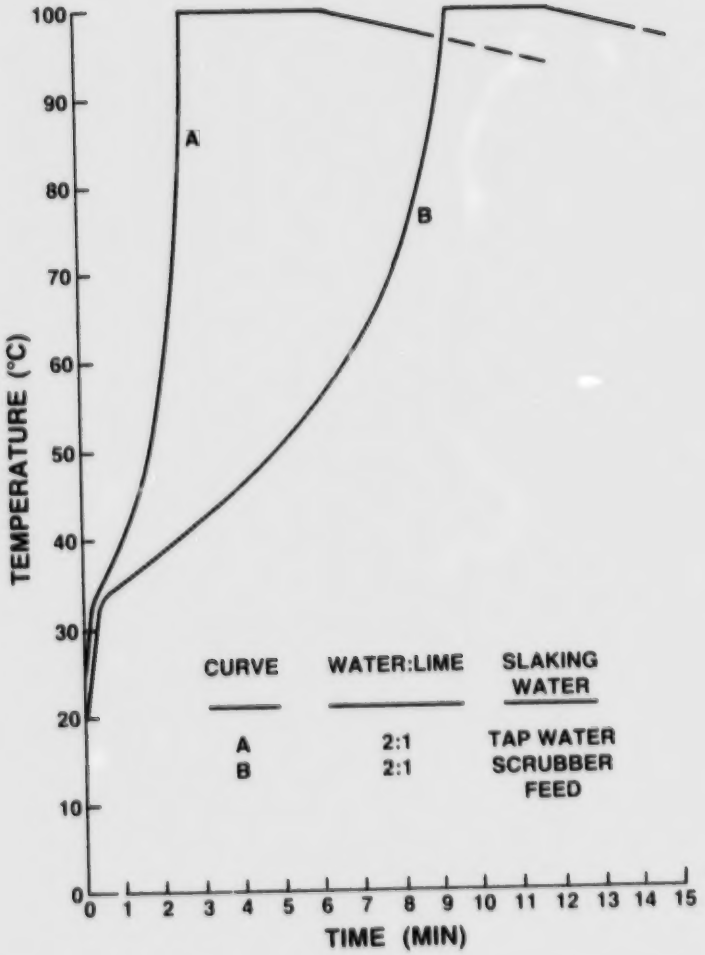


FIGURE 17 SLAKING RATE OF LIME WITH TAP WATER AND SCRUBBER FEED

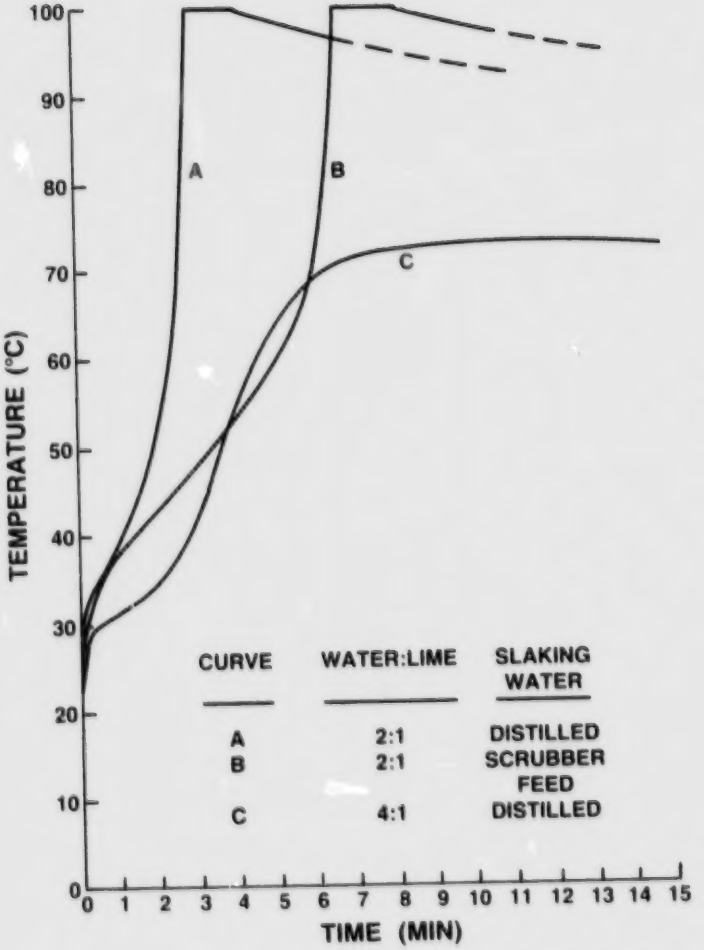
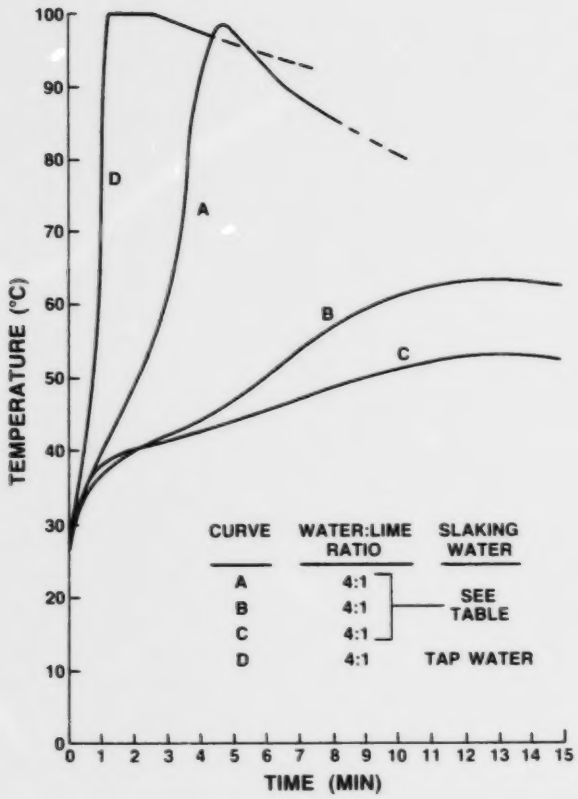


FIGURE 18 EFFECT OF LIQUID-TO-SOLID RATIO ON SLAKING RATE OF LIME



PARTIAL WATER ANALYSES (mg / L)

Ion	Curve A	Curve B	Curve C
Ca^{++}	30	20	50
Mg^{++}	2200	2100	3100
$SO_3^{=}$	1780	2350	1230
$SO_4^{=}$	5400	4800	6300
Cl^{-}	800	800	900
$CO_3^{=}$	140	280	280

FIGURE 19 EFFECT OF WATER QUALITY ON SLAKING RATE (12)

The work of Kunesh (28) confirms that of Baker and Jordan (27). The retardation of slaking appears to be due to the rapid formation of insoluble coatings of calcium sulphate and calcium carbonate on the surface of quicklime particles. Scanning electron micrographs (SEM) of these surface coatings reveal that a high level of crystallization occurs during slaking. These coatings apparently prevent contact between the pore structure and the slaking water. SEM examination of liner materials by Grimshaw et al. (1) also identified the presence of such crystals on liner materials exposed to AFBC synthetic leachates.

2.4.2 Data Gaps. Gaps still exist in the understanding and quantification of the exothermicity of AFBC residues. These limit the development of a rational approach to the handling and disposal of this type of material at this time.

Theoretical basis. Description of the reaction of residues from bubbling AFBC with water relies heavily on experience and theory in lime slaking. The theory has

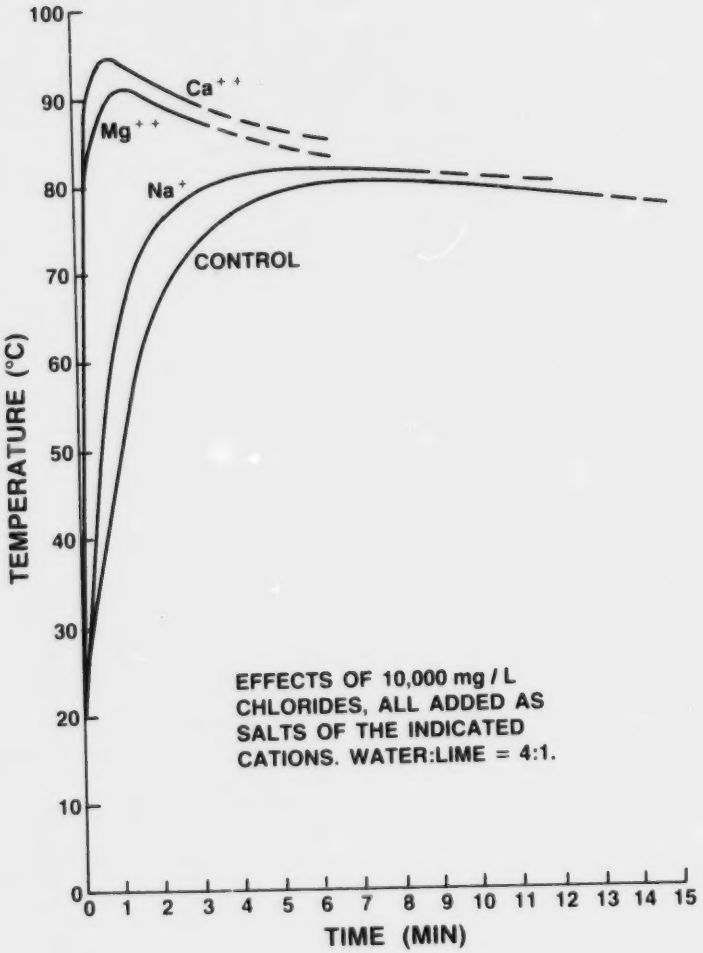


FIGURE 20 EFFECTS OF SULPHATES ON SLAKING RATE OF LIME

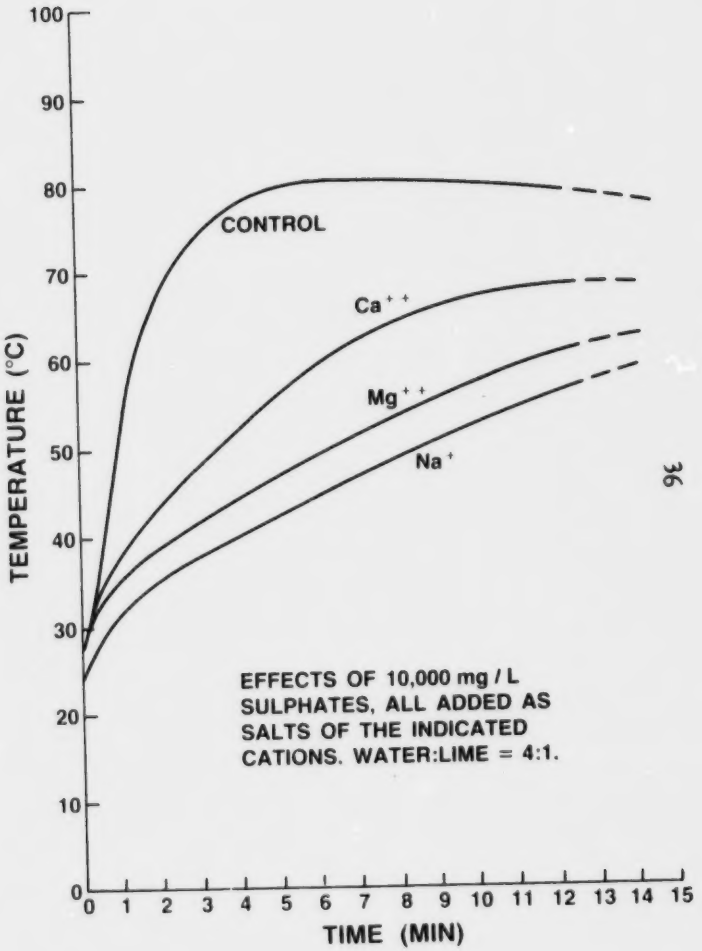


FIGURE 21 EFFECTS OF CHLORIDES ON SLAKING RATE OF LIME

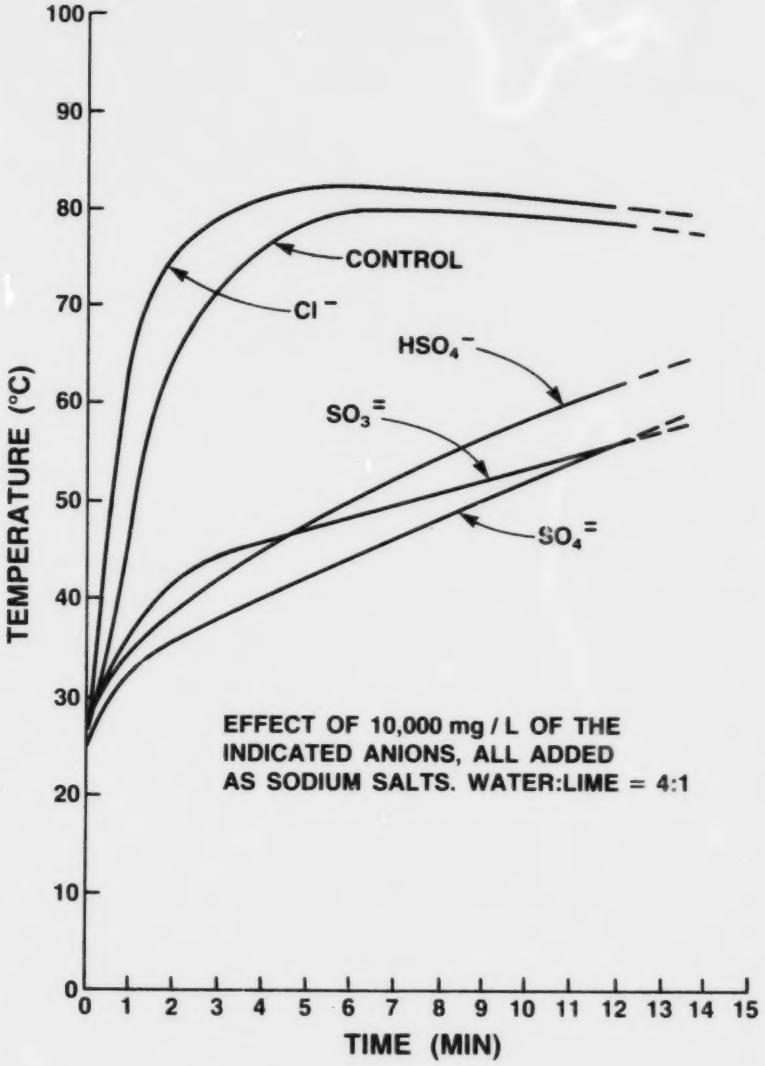


FIGURE 22 EFFECT OF ANIONS ON SLAKING RATE OF LIME

progressed relatively recently, probably because of the development of sophisticated analytical techniques such as scanning electron microscopy. A significant assumption, namely that lime-slaking theory is directly transferable to AFBC wastes, has also been made even though bubbling AFBC residue is a mixture which includes calcium oxide and other components. But the effect of the other crystalline and amorphous substances on the applicability of lime-slaking theory still needs to be addressed. Hot, violent chemical reactions have occurred at times during the slaking of this material; while at other times, under apparently similar conditions, quite different reactions have occurred with the same

materials. Since this apparent unpredictability could affect safe waste-handling and disposal options, the governing mechanisms must now be defined further, so that they can be controlled.

Surface area. One of the governing factors in the reaction of calcium oxide with water appears to be the surface area and porosity of the lime particle. Further testing is desirable to determine whether surface area is, in fact, a significant parameter in AFBC residues in describing their reactivity. A rapid measurement of this property might also be useful in classifying the reactivity of AFBC residues in the field.

Test protocol. Although the reactivity of AFBC residues has been demonstrated, the procedures used have been developed for application in laboratories. For day-to-day disposal, a practical, rapid test method applicable in the field is needed to alert operators to highly reactive residues batch by batch or truck load by truck load. This would facilitate decisions on use of special handling precautions.

Refinement of a calorimetry procedure for FBC waste-testing similar to the ASTM method would also be beneficial. Such a method would need to take into consideration the wide variety of residues which might be encountered during testing. Comparison and evaluation of the properties of the waste is now difficult because a range of methods and liquid-to-solid ratios is used. The test procedure should also provide information on the rates of reaction which can be expected.

Column testing. Emphasis has been placed on quantifying the properties of AFBC residues with a high calcium oxide content from the perspective of a chemical reagent rather than from that of material for waste disposal. Therefore, results of calorimetry and column testing have not always been comparable. Two paths are possible to resolve this problem. A model for comparison and extension of the results of these two methods of testing can be advanced and refined. Alternatively, a more refined procedure to study the slaking of combustion residues in situ at low liquid-to-solid ratios could be developed.

Effects of released heat on liner material. The exothermic reaction of AFBC residues with water could have a great impact on the type and durability of liner materials which might be used at a disposal site. Liners could be exposed to temperatures significantly greater than ambient temperatures due to the heat release from the slaking of calcium oxide in the combustion residues. The heat may damage synthetic liner materials and possibly dehydrate clays. Subsequently, either clay or synthetic liner materials would also encounter alkaline leachates. The combined effects of these factors on liners require further evaluation.

Control of heat release with water quality. Some results indicate that the anions in the water used for slaking can either accelerate or retard the chemical reaction during slaking. In one case, the maximum temperature rise was reduced by about 50°C. If this same effect holds for AFBC wastes, the heat release could be greatly reduced and better controlled by using certain low-quality wastewaters (high sulphate and TDS concentrations) from other sources at the combustion site or by using water with chemical additions. This would reduce both the hazard level of the residue and the volume of wastewater to be treated.

Slaking of aged wastes. Some technical literature suggests that the reactivity of aged samples is much less than that of fresh samples. This is likely due to the reaction of the calcium oxide content of the ash with water or carbon dioxide from the air over an extended period. Particle agglomeration is also possible. The practicality of letting AFBC residues age to reduce the reactivity of the residue has yet to be investigated. However, based on the current understanding of this type of residue, storage of the unconditioned waste, high in calcium oxide content, in a large mass in a confined space is not advised. This is due to the potential for exothermic reaction, possible swelling, and in situ strength development, if contact with and penetration by water occurs.

2.5 Engineering Properties

This section summarizes the properties of AFBC residues which would affect its handling and disposal properties. Emphasis is placed on the bulk properties rather than those of single particles. In general, test procedures used to date for these residues have been adapted from soils testing or geotechnical engineering practices, both designed to use relatively large samples.

2.5.1 Relevant Data For AFBC Spent Bed Material and Carryover.

Stone and Kahle (4) determined some of the physical properties of spent bed material and carryover from an AFBC combustor (see Table 3).

Bulk density. The bulk density of the spent bed material was greater than that of the fly ash. The initial bulk density of the fly ash remained at 0.76 g/cm^3 after slaking, whereas the bulk density of the bed material increased slightly from 0.92 to 0.97 g/cm^3 after slaking. However, this increase in bulk density does not appear to be consistent. Pope et al. (cited in (4)) reported that the dry density of one spent bed material decreased by 49 percent after slaking, whereas another increased by 48 percent.

TABLE 3 PHYSICAL PROPERTIES OF AFBC SPENT BED MATERIAL AND CARRYOVER/FLY ASH (9)

Property	Spent Bed Material	Carryover/Fly Ash
Specific gravity[a] (g/cc)	2.8	2.65
Moisture content[b] (% dry wt.)	0	0
Degree of saturation[b] (% dry wt.)	0	0
Dry density (g/cc)		
• before slaking	0.92	0.76
• after slaking	0.97	0.76
Water-holding capacity[a] (g H_2O/g residue)	0.44 - 0.98	0.66
Permeability (cm/s)[a]	6.8×10^{-4} - 3.7×10^{-2}	1.9×10^{-3}

Notes: a = after slaking
b = before slaking

Dry density/moisture content. Integ (29) reported results of dry density /moisture content testing conducted on AFBC waste generated by a British coal and limestone. Dry density/moisture content relationships were established for material compacted into a 102-mm cube with a vibrating hammer. After curing in molds for 7 days, the unconfined compressive strength/time relationships for these formed cubes were established by the use of a 180-tonne concrete-testing machine with a loading rate of 2 N mm^{-2} min^{-1}. From an initial density of 1300 kg/m^3 in the dry condition, the ash showed a considerable reduction in dry density when small quantities of water were used in the formation of the compacted cubes. This effect was probably due to the initial reaction of free water with the lime, combined with an expansion of the solid phase. As the moisture content was increased, a maximum density was achieved followed by a gradual reduction. The peak density of about 1450 kg/m^3 was achieved with a water content of about 30 percent.

Water-holding capacity. The water-holding capacity (i.e., the amount of water that can be retained against the force of gravity) was 66 percent for the fly ash and 44 to 98 percent for the spent bed material.

Permeability. The permeability of the bed ash ranged from 6.8×10^{-4} to 3.7×10^{-2} cm/s. By comparison, the permeability of gravel is approximately 8.2×10^{-2} cm/s, indicating that the spent bed materials are quite permeable. However, it has been

suggested that these permeability coefficients, which were determined in short-term laboratory tests, may not be indicative of long-term field disposal situations because of changes in the disposed ash. Some reduction in water permeability, possibly up to 50 percent, may occur in the ash after a period of 1 or 2 weeks (29). Minnick (30) reported that the permeability increased on average from 1.145×10^{-3} initially to 2.19×10^{-3} cm/s after 28 days.

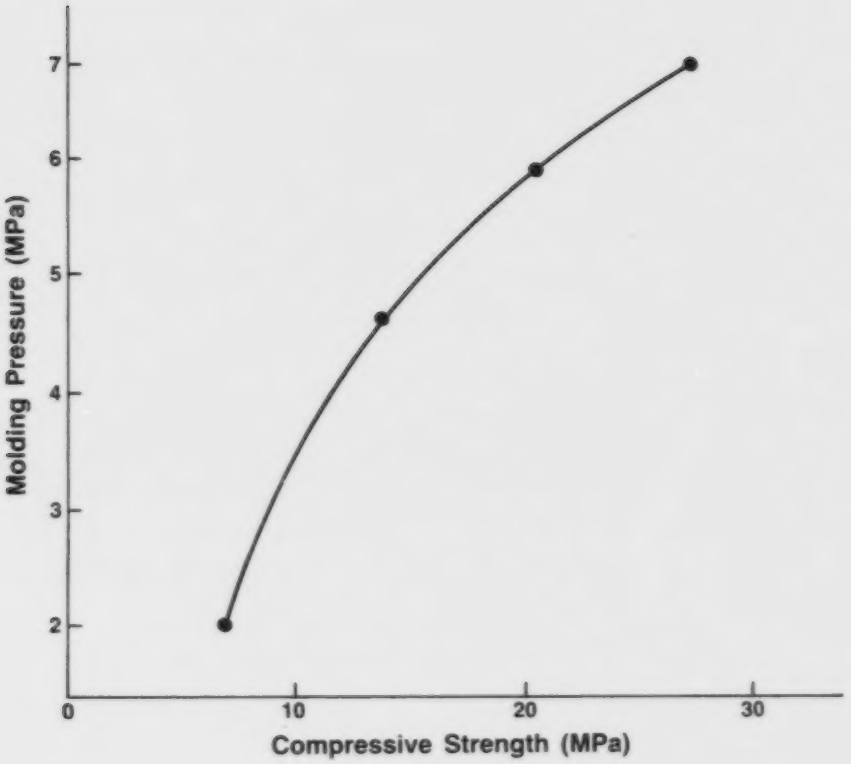
Cementing value. The cementing value of an AFBC waste was also reported (28). The relationship between molding pressure and compressive strength, and compressive strength and moisture content are shown on Figure 23. For these tests, a maximum compressive strength of 28 MPa (4000 psi) was achieved with an 5.5 MPa (800 psi) moulding pressure. Maximum compressive strength of about 7 MPa (1000 psi) was developed when the residue contained 35 percent moisture. The engineering properties of AFBC spent bed material are shown on Table 4 (30). Although the analyses are thorough, they represent the testing of a limited number of samples from one combustor. Thus, their representativeness is questionable.

TABLE 4 ENGINEERING PROPERTIES OF AFBC SPENT BED MATERIAL*

Property	Procedure	Parameter	Value
Compaction	ASTM D1557-70	Maximum dry density	109 pcf
		Optimum moisture	15.7 - 18.9%
Unit weight	ASTM D29	Dry rodded weight	77.1 pcf
		Loose unit weight	72.4 pcf
Atterberg limit	ASTM D423--66 & D424-59	Plastic limit	non-plastic
		Liquid limit	34%
		Plastic index	non-plastic
Direct shear on cohesionless soil		Average ultimate angle of friction	31.3°
		Average dry unit weight	108.4 pcf
		Average moisture content	19.4%
California bearing ratio+	ASTM D1883-73	Dry density	91.6 pcf
		Initial moisture	13.2%
		after test (top 1)	26.1%
		Swell	.45%
		Bearing ratio 0.10	82.8%
		0.20	87.8%

* Spent bed material from the Alexandria unit

\+ Average of three values



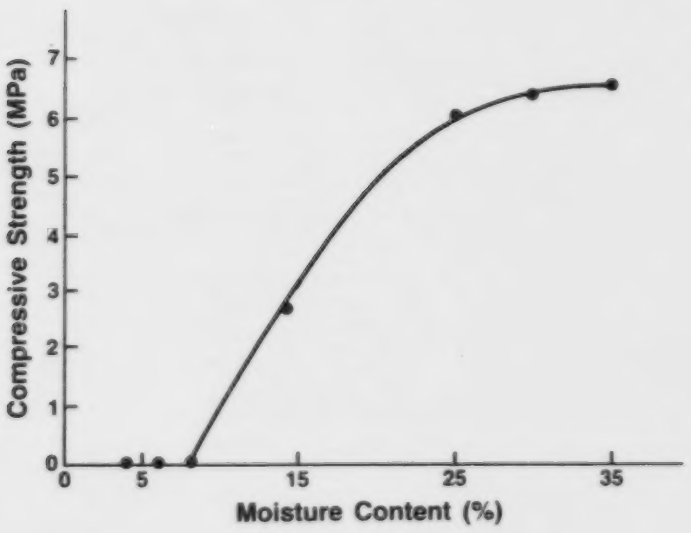


FIGURE 23 CEMENTING VALUE OF AFBC WASTES

2.5.2 Relevant data for AFBC residues from bubbling-bed facilities. Dearborn (5) reported the physical properties of AFBC residues produced at small bubbling-bed facilities where eastern Canadian high-sulphur coal was burned with eastern Canadian limestone. These results are listed in Table 5. The first three AFBC solid residues listed were in storage for several years and samples were occasionally removed before this characterization. Consequently these materials were not continuously under seal during all of this period. Therefore, opportunities for the humidification and carbonation of some portions of these samples occurred as a result of occasional exposure to the atmosphere. Thus, it is possible that the tested spent bed materials exhibited some properties different from those of fresh, properly stored samples.

Also listed in Table 5 are the results of subsequent testing of similar fresh samples from the Queen's University pilot plant and the heating plant at Summerside.

TABLE 5 PHYSICAL PROPERTIES OF BUBBLING AFBC RESIDUES

Combustor	Coal	Residue	Moisture Content (%)	Specific Gravity (g/cm^3)	Water-Holding Capacity (%)	Permeability (cm/s)
Test Unit	Minto	Bed	0.0	2.82	48	2.2×10^{-2}
	Devco	Bed	0.1	2.93	63	2.5×10^{-2}
		Carryover	5.4	2.80	145	3.3×10^{-5}
Queens	Evans	Bed	0.0*		62.4	
		Cyclone	0.03		72.8	
		Carryover	0.43		88.9	
Summerside		Bed	0.0*		39.4	
		Carryover	0.07		77.2	

* Bed material samples were hygroscopic when heated

Moisture content. The moisture content of all materials was less than 1 percent, with one exception attributable to improper sample handling and storage. Thus, the properties of residues described are those of materials which have not been in contact with water. Different properties might be expected from residues which were exposed to

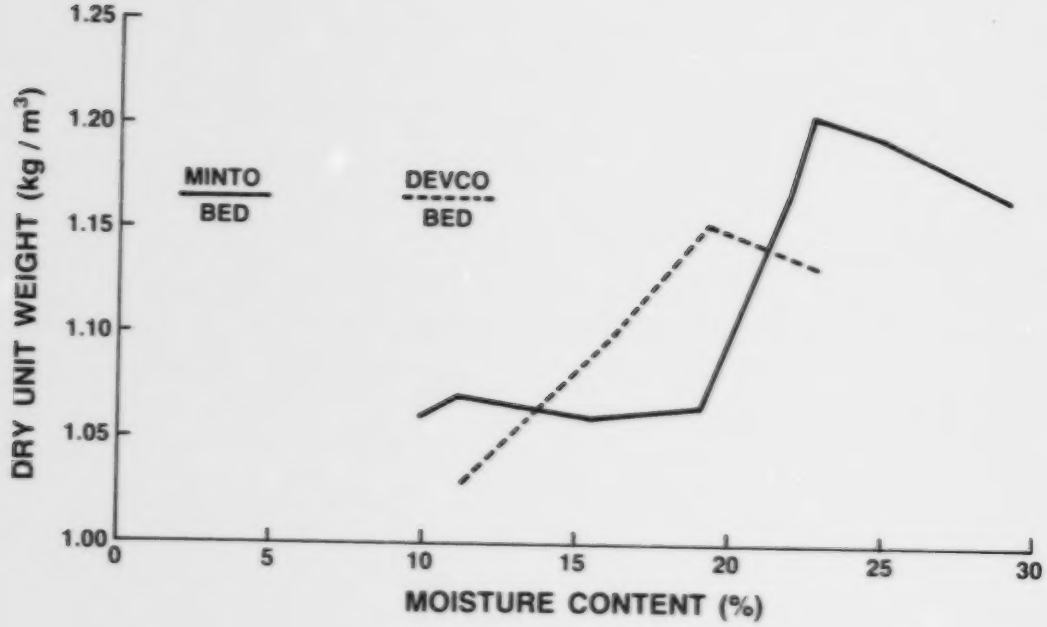
the atmosphere or slaked and then subjected to these tests. The specific gravity of the residues ranges from 2.80 to 2.93 g/cm^3, which compares favourably with previous results reported by Stone and Kahle (4). The values are slightly greater than the average value suggested for soil, which is about 2.65 g/cm^3.

Water-holding capacity. The water-holding tests indicate the amount of water the residue can retain under the force of gravity. The physical mechanisms affecting water retention are complex; however, the results suggest how much water is required to wet the residue and how drainable the waste would be. The bed materials in this test had lower water-holding capacities than the carryover. In general, the residues can be expected to retain an amount of water equal to between 40 and 145 percent of their own weight. This would suggest that the handling and draining of the residues at a disposal site would be a significant design concern, if the material were handled in a wetted form.

Permeability. The coefficients of permeability of the two bed materials were approximately the same at about 2.4×10^{-2} cm/s, and are at the upper limit of the range of 3.7×10^{-2} to 6.8×10^{-4} cm/s reported by Stone and Kahle (4) for AFBC spent bed materials. The coefficient of permeability of the baghouse material, at 3.3×10^{-5} cm/s, is three orders of magnitude less than that of the bed materials. It is significantly less than the value of 1.9×10^{-3} cm/s reported by Stone and Kahle for AFBC carryover/fly ash. For comparison, clean medium sands have permeability coefficients in the range of 10^{-2} cm/s, and are classified as moderately permeable. Values in the 10^{-5} cm/s range are typical of silty sands and sandy clays.

Dry density/moisture content. The results of compaction testing on the three residues over a range of moisture contents are shown in Figure 24. The maximum dry densities of the bed materials were achieved at about 20 percent moisture. For the baghouse materials, no maximum was reached over the ranges of moisture content used in the tests. The maximum density to which a material can be compacted depends on the amount of energy applied during compaction and the moisture content of the material. This is important in disposal area design, because disposal volume requirements decrease as waste density increases. Furthermore, the shear strength of a material generally increases as the degree of compaction increases. The test results suggest that the bed and baghouse materials are very different in terms of the amounts of water they require to maximize their densities and thereby minimize their requirements for disposal volume.

Swelling and shrinking. One property which has apparently received little attention in characterization studies is the swelling or shrinking of combustion residues when wetted. Presumably the calcium oxide in the residues would expand when slaked.



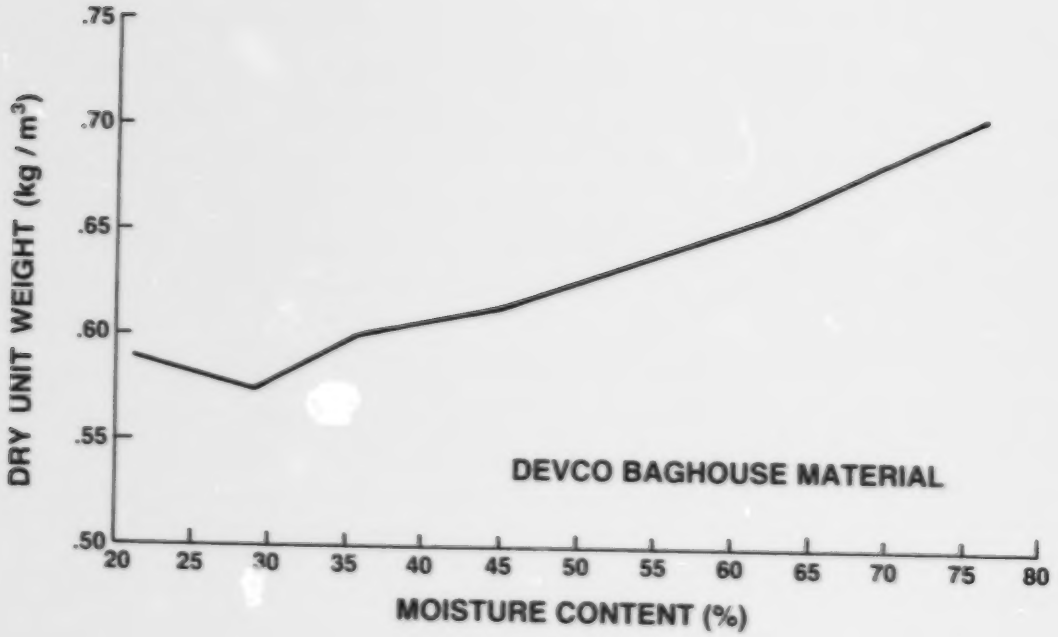


FIGURE 24 MOISTURE CONTENT vs. DENSITY

Thus, slaking could cause a volumetric increase in the amount of waste. Dearborn (5) reported that during column exothermic testing, the bed materials appeared to expand by about 10 percent in the confines of the column following the addition of water. Visible swelling during slaking tests has been observed a number of times. Similarly, in other static column tests, expansion of the material reportedly fractured plastic columns (26). However, the information on swelling to date is only descriptive. Quantitative data on when and how swelling occurs is now desirable. ASTM (21) cites a procedure for testing the expansion of hydrated lime when autoclaved. This approach could be used as a starting point to develop an AFBC residue-specific testing procedure.

Cementing properties. Berry (31) investigated a wide range of soil cementing properties of AFBC residues from the Summerside, P.E.I. combustor. In reviewing the work of other investigators of the engineering properties of AFBC residues, he indicated that the residues exhibit the ability to form a cemented mass and this was generally attributed to the hydration of lime. However, the hydration of anhydrite ($CaSO_4$) may contribute to the cementing action as well. Lime itself does not normally form cementitious bonds except after considerable exposure to carbon dioxide. Calcium sulphate on the other hand is a well established non-hydraulic cement (31).

Substantial cementitious strength may be developed by AFBC residues upon reaction with water. When the moisture content is increased from 12 to 35 percent, substantial increases in strength have been obtained. This is contrary to the usual behavior of 'cements' and indicates that the residue has a large demand for water of hydration (31). However, because the cementing activity originates with the reactions of calcium sulphates and calcium oxide, AFBC residues cannot be expected to function as hydraulic cements. That is, they cannot be expected to form cemented masses when immersed in water as does Portland cement, nor should the cemented products from AFBC wastes be expected to be very stable when used in water-soaked situations (31).

Behaviour of soil-cement mixes. Although the work of Berry (31) is preliminary, some general observations on the effects of AFBC residue on the development of soil strength were made. Soil blended with spent bed or carryover materials, or both, and with Portland cement, at concentrations similar to those used in soil-cement, showed increased load-bearing capacity as well as improved resistance to freeze-thaw and to expansion.

In a follow-up study Berry (31) further evaluated the behavior of soil-cement mixes, using combinations of AFBC ash from the Summerside unit and Portland cement. In his previous experiments (32) he found that soil/Portland cement/AFBC residue mixes

did not develop the expected level of compressive strength even when cured for 28 days. He suggested that this may have resulted from the manner in which the curing had been conducted, which in effect prevented access of sufficient water to the specimens to permit the complete hydration of lime, anhydrite, and Portland cement. It was suggested that if either the waste were preconditioned with enough water to hydrate the lime and the anhydrite, or if curing were performed under circumstances allowing access of water to the specimens, this problem could be avoided. Further, he recognized that any preconditioning or curing procedure used in the laboratory must be selected with regard to the practical limitations that control field application of soil-cements. In practice, he concluded, the excessive heat of reaction due to the slaking of calcium oxide in the residue renders the process of preconditioning unsafe in the laboratory and impracticable in the field. It was suggested that an alternative mode of preslaking would be to follow the practice of the lime industry and use excessive water. This was recognized as impractical for field application, and further efforts to precondition the residues were therefore abandoned. It was decided to permit the hydration of the waste-soil mixture to occur in the Proctor tests before compaction. Optimum moisture would then include both water for slaking and water for compaction.

Specimens were cured in a moist room in open containers, using paper towelling covers to protect them from direct impact of water droplets. Using this protocol, the compressive strengths of the mixes increased to between 2.0 and 2.5 MPa compared to previous values of between 1 and 1.75 MPa. Hydration of the cement component must be complete for this strength development.

Standard Proctor tests, modified only to the extent described above to permit prehydration of the ash, showed that adequate compaction and densification of the materials was possible at optimum water contents of 12 to 13 percent. Compacted dry densities of 1850 to 1975 kg/m^3 were attained (32).

Strengths in the range of 2 to 2.25 MPa were attained for mixes of 7.5 percent ash, 85 percent soil, and 7.5 percent cement. Ash and soil mixes did not attain suitable strengths in the absence of Portland cement; i.e., values close to 0.3 MPa were reached. Such levels of strength development might be acceptable for disposal purposes, but not for road base or sub-base construction (32).

Cured ash-cement-soil mixes expanded by 0.9 to 1.3 percent when measured with a test apparatus permitting expansion in only one dimension. In addition it was observed that the mixes were not durable when exposed to freeze-thaw cycles. The Portland Cement Association (33) recommends that for adequate field durability, a soil-

cement specimen should not lose more than 14 percent of material during 12 cycles of freezing and thawing in standard tests. The specimens tested showed losses greater than 30 percent.

2.5.3 Data Gaps. With regard to the engineering properties of AFBC residues as they relate to safe disposal, some data exists for samples from one U.S. pilot plant, presumably for a limited range of coal and sorbent types. Other information from initial studies tends to be contradictory. For example, one researcher speculates that the hydraulic conductivity of the residues would decrease with time, whereas another notes an increase with time. The differences could be attributed to a variety of factors, including the test procedures used (slaking and mixing), the history of the sample, or characteristics of the coal and sorbent type used. They could also be interpreted as indicating the reactivity of the material and variability of the product under different reaction conditions.

Canadian data is limited so far. Research in the area of soil-cement and soil strength development has been conducted using residues produced under Canadian conditions, but the intent of this work was to examine the use of the residue for construction purposes. Poor strength development properties were indicated, suggesting that the residues would be useless for the construction of road beds. However, the properties may be adequate for non-load-bearing application at environmentally sound disposal sites.

In general, the properties of this waste have not as yet been thoroughly quantified from the perspective of disposal area design. In view of the contradictory evidence of reactivity and variability in the product from the reaction, this is understandable. The existing information suggests that the residues can solidify upon reaction with water, under some conditions. The development of a crust and strength in a disposal area can be seen as benefits, particularly in terms of fugitive dust control, reduced leachate production, and rearrangement of deposited material before the disposal area can be capped and reclaimed. The stability of the deposited material or the stability of dry, partially slaked or completely slaked materials over a long time, is not known. Whether these materials will shrink, expand, or dry out in the long term still remains to be determined. Disposal areas and leachate control systems must be designed for worst-case conditions over the life of the disposal site. It is not yet known whether the worst case occurs when the material is first deposited or at much later time. Consequently, until more is known about the long-term stability of these materials, optimized disposal area designs cannot be developed.

The potential for this residue to swell on contact with water has also been indicated in laboratory studies. Swelling could develop significant pressures in confined areas, and could damage handling equipment or affect the integrity of liner materials in disposal sites. No widely used test procedure appears to exist to quantify this property. However, an ASTM procedure exists which could be used as a starting point for the development of a protocol of this nature.

3 FIELD EXPERIENCE

3.1 General

Due to the short history of the commercial AFBC process, the experiences of AFBC operators are necessarily limited at this time. There are fewer AFBC units than conventional PCF plants, and they are still much smaller than utility-scale PCF plants. Similarly, in the various plants, designs are still being optimized. To date, the approaches to waste management for bubbling AFBC wastes have, in general, been adapted from PCF or municipal landfilling practices, with subsequent modifications to suit the individual handling problems and site conditions as they arise. In short, development of optimum disposal means is still very much an active and ongoing process.

3.2 Existing Fluidized Bed Plants

At this time no large (150+ MWe) coal-fired AFBC power utility plants are operating in North America. Bubbling-bed demonstration units, institutional steam plants, and industrial steam plants are, however, operational across the United States. In Canada, only one production unit at present is at the Summerside P.E.I. Canadian Forces Base. Another unit, of newer circulating FB design (22.5 MWe), was scheduled for startup in New Brunswick in 1986. This circulating design is expected to produce wastes of somewhat different characteristics than the bubbling-bed wastes examined to date.

A listing of current coal-fired AFBC installations in North America, taken from Schweiger (34), is given in Appendix A. The diversity in plant size is considerable. However, compared to conventional steam or power plants, the actual number of stations of interest for this study is quite limited, also in scale, variety, and duration of experience.

3.3 Industry Waste Disposal Practice

In most cases, waste disposal practice is still under development or being carried out on an ad hoc basis. With demonstration units, disposal often takes place on-site or in a convenient location nearest to the generation site. Several variations in approach have apparently been, and are still being, tried. It also appears that further variations will continue to be tried in the near future as newer designs and larger units are developed.

CFB Summerside heating plant. This plant is composed of two Foster-Wheeler Corporation bubbling-bed units of 18-Mg/h capacity each, or 36-Mg/h total steam

capacity. It is fuelled with bituminous coal of about 27.9 MJ/kg (12000 BTU/lb) and containing about 20 percent ash and about 5 percent sulphur. The sulphur-absorbing medium, Havelock limestone, is excellent material for this purpose. The characteristics of the fuel, sorbent and ash have been discussed in previous works (5 et seq.). The limestone sorbent is used to provide a calcium:sulphur molar ratio in the 2:1 to 3:1 range.

Target sulphur removal is 90 percent, or an emission rate below 1.64 kg/10^6 kg of SO_2·kJ (1.64 lb/10^6 lb of SO_2/BTU) or less. Design fuel is Cape Breton coal of 20 percent ash, 5.5 percent sulphur, and 26.7 MJ/kg (11 500 BTU/lb).

Currently, both fly ash and bed ash are conveyed to a silo which can hold the ash from 3 days of production. The ash is dropped from the silo through a pneumatically activated gate valve and chute into a tank in the bed of a dump truck. This procedure is intended to minimize dust during loading of the truck.

The ash is carried by the truck to the disposal site about 1 km away. It is dropped into a trench by opening a gate at the back of the tank and tipping the dump truck. Dust may be generated during release. Operators use dust masks and goggles when exposed to the airborne ash. No waste conditioning is routinely done before dumping. Spraying to reduce dust in dry weather may have been employed. Normally, the ash in the trench forms a surface crust within a day from exposure to humid atmosphere or rain. This limits fugitive dust emissions. In addition, filled ash trenches have been covered with soil.

An indication of the reactivity of the waste material is given by one reported incident in which, through improper operational procedures which permitted entry of moisture, baghouse ash solidified in the bags during a summer shutdown. Similarly, steam generation has been demonstrated from Summerside ash/water reactions in the laboratory on a number of occasions. On standing, this ash eventually forms monolithic blocks amenable to breaking and moving by bulldozer in the trenches where it was dumped.

Georgetown University. The Georgetown University unit is of design similar to that at Summerside, but with several years more in-house development and modifications. It is rated at 45.5-Mg/h (100 000-lb/hr) steam capacity, using coal of 27.9 to 30.2 MJ/kg (12 to 13 000 BTU/lb) containing 8 percent ash and 3.3 percent sulphur. The limestone used is of local agricultural grade, and the design calcium-to-sulphur ratio is 3:1. Emissions are expected to meet the Washington, D.C. limit of 0.34 kg SO_2/GJ (0.78 lb of SO_2/million BTU). Bed and fly ashes are collected in a silo. The discharge of the silo is indoors, whereas the silo in Summerside is outdoors. Ash is dropped from a silo through a chute into a dump truck with a dust-tight aluminium cover. Ventilation at the

chute controls dust. It is then hauled away. The staff report no problems in handling or loading the ash by this method; no problems have been reported by the haulers either.

The ash has been used by a sand and gravel firm in its operations. No data on actual disposal is therefore available. Georgetown University monitors the health of employees working with AFBC residues regularly and to date no problems have been reported. Goggles and respirators are provided for use in dusty conditions.

Shawnee Power Station AFBC pilot plant. The Tennessee Valley Authority pilot plant at the Shawnee station is a bubbling-bed unit, built by Babcock Wilcox, and rated at 20 MW or 50 Mg/h (111 000 lb/hr) steam. Fuel is Kentucky No. 9 coal, containing 12 percent ash, and 3.5 to 4.5 percent sulphur, with a heat value of 25.6 to 27.9 GJ/kg (11 to 12 000 BTU/lb). The calcium-to-sulphur ratio target is 2.3:1. The sulphur capture target is 90 percent, equivalent to 0.52 kg SO_2/GJ (1.2 lb SO_2/GJ million BTU) the U.S. EPA limit.

Bed ash and fly ash are handled from separate silos. Bed ash is easier to wet, as it is less prone to either dusting or liquefying under mixing conditions. Bed and fly ash are deposited in separate piles, since on-site uses have been found for the bed ash.

At present, water is added to the ash from the unit prior to disposal. The objectives are to eliminate dust and produce a material of soil-like consistency. The ash is dropped from a hopper to one end of an open trough-like chamber. It is conveyed from the hopper end to the dropout end by two rotating shafts which for fly ash have paddle attachments; and for bed ash, ribbon conveyors. Water spray nozzles wet the ash as it is stirred and conveyed to the dropout.

From the dropout it falls to a dump truck. The mixture becomes quite hot; steam is produced at the mixer and in the truck.

The operator controls ash and water flow visually: increasing the amount of water when the ash becomes too dry and dusty, decreasing it when it is too fluid. Because the operation can be dusty, goggles, respiratory protection, and protective clothing are routinely worn. When the truck is nearly full, the hopper is run out. If material is left in the hopper, it will solidify on standing to a concrete-like mass. It is necessary to chip the conditioning unit free of "cemented" material periodically or it will become unusable.

The disposal site is a few hundred metres from the silos, so the disposal trip takes less than 10 minutes.

The truckload of ash is driven over previously deposited ash and dumped. When enough ash has accumulated, it is shifted over the edge of the mound by a bulldozer.

The consistency of both fly and bed ash piles thus compacted appears to be somewhat like concrete.

Uncompacted material is loose and friable. Apparently driving on the material in winter is satisfactory. No problems with traction were reported. Although winter temperatures as low as (-18°C) occur in January, it is not known whether the duration is sufficient to produce freeze-thaw cycles deeper than a few centimetres into the ash.

The staff observed that the ash mass steams vigorously as it is being transported to and dumped at the disposal site. The wetted ash may again become dry after dumping, due to moisture loss caused by the heat release from the continuing reaction. Drying of fresh, conditioned ash even during a rainstorm is quite apparent. Under a moist, dark crust, the ash appears light and powdery. In such cases, it is again "wetted down" with water from a sprinker truck.

Industrial boiler operator (A). This company operates a number of 22 700 kg/h (50 000-lb/hr) bubbling-bed AFBC units at several sites. Their practice at most sites is to convey dry ash from silos (mixed ash) by covered dump trucks to landfill sites. The trucks hold 18 tonnes of ash; the hauling distance is 30 to 60 km, depending on location. Dust is not a problem in loading, because a coaxial ash chute and dust capture system is used. Dust does become a problem when the trucks unload; protective equipment is used by operators. Conditioning to reduce fugitive dust emissions is required at one site. Dust is their immediate problem regarding disposal, since local government legislation is forcing the company to carry out dustless disposal.

The ash produced is exothermic; tests reportedly show that mixing water and ash in a 1:1 ratio (weight) raises the temperature to 100°C, so that steam is produced.

The company has explored several approaches to ash disposal besides hauling the ash dry to the disposal site. They include:

- Dumping the dry ash into a pit, spraying it with water to condition it, and hauling it out for disposal later. This is effective, but requires multiple handling of the ash.
- Mixing the ash in a concrete-mixer truck. Tests have indicated that excessive heat buildup to over 100°C occurs when-mixing water and ash in a 1:1 ratio (weight). Mixing is accompanied by steam and violent ejection of wet ash from the mixer (described as "like a volcano") and severe vibration of the mixer as the ash and water in the mixer react.
- In addition to the heat problems, hauling wet ash is more expensive. Hauling costs could be doubled if a 1:1 water and ash mixture were transported in conventional

trucks; costs for a concrete-mixer truck would be still higher. Ash treated this way could also solidify in the mixer, causing considerable difficulty in cleaning.

- Mixing ash and water in an inclined, rotating conditioning drum. Mixing and conveying are accomplished by drum rotation and a stationary internal scraper blade. Ash is conveyed by an Archimedes screw into one end of the drum, and an equal amount of water is sprayed onto it over the length of the drum. Considerable amounts of heat and steam are generated. The steam escapes through the open ends of the drum. Wet ash, in consistency like wet concrete, drops to a holding pad below. It is left to cool and harden for 1 or 2 days, and then loaded onto a dump truck with an overhead loader and hauled to the disposal site. To haul the ash immediately after conditioning is not considered practical, as it is very hot and, besides, does not dump cleanly from the truck at the disposal site. If it is allowed to sit much longer, it hardens too much to break readily enough to be scooped up with the loader. This procedure has been satisfactory, because it solves the problems of dust, exothermicity, and solidification in the truck.

Daily ash production at this facility is about 15.4 tonnes. The conditioning of that ash takes a few hours each day. The conditioner is reportedly easily cleaned if hosed out immediately after use. If the wet ash is allowed to remain in it, it will harden and become difficult to remove. Scale-up of the conditioning unit may be feasible for larger plants.

Industrial boiler operator (B). This plant hauls wet ash by concrete-mixer truck having a 5-m^3 (7-cu. yard) capacity. First, the mixer is half-filled with water and rotated. Ash is added from a silo for a predetermined time to produce a fluid mass that is not too hot. But an excess of ash reportedly causes the mixture to boil and be ejected from the mouth of the mixer. Normally, 10 loads are hauled every shift. The ash is dumped into a large ash burial pit a short distance from the plant. It can be driven upon when dry (after a few days) or moved around by bulldozer. The mixer must be washed out after each dump to prevent setting of any remaining material. This practice is not used in winter since temperatures are well below the freezing point and the plant is not equipped to water-treat in such conditions. Ash is hauled and dumped dry when water cannot be used. Under these conditions, considerable dust is generated. Dumped wastes have solidified since deposition.

The concrete mixer truck is not considered an ideal way to haul this ash. The hauling costs are high because the cement truck has a relatively low capacity and many resources in equipment and manpower are needed.

Coal-waste-burning plant. Ash was originally hauled dry by dump truck to a landfill site, but dust problems at the site reportedly led to a search for another method.

The current practice is to load ash from the silo into a closed pneumatic tanker and discharge it pneumatically into a water-filled quarry pit, about 2 m under water. If the discharge tube is submerged enough, no dust is generated. The truck is loaded from a feed pipe with a built-in dust control system, so that protective equipment is not normally needed. So far, this plant has had no experience with this method during winter.

The plan is to dig out and landfill the ash when the pond is full, which will not occur until some time in the future because of its large capacity. The hauling distance to the pit is a few kilometres.

Industrial boiler operator (C). Ash is taken by screw conveyor from a silo to a covered truck, which hauls it to a landfill pit 11 km away. No problems with this disposal method were reported. However, the process is sufficiently dusty to produce maintenance problems, so that conditioning for dust control has been tried. Conditioning with water in a screw conveyor has reportedly been unsatisfactory because the setting rate of the ash apparently made such a process impractical. As an alternative, maintenance procedures have been modified to counteract the effects of the dust on machinery wear and the consequent breakdown rates.

Dust control at the disposal site has apparently not become an issue yet.

3.4 Common Factors in Disposal

3.4.1 Dust. The major stated concern regarding dust appears to have been that dust generation makes the ash unacceptable at landfills, especially those close to residential or commercial areas. Some operators of landfill sites who have initially accepted the ash later refused it. Such refusals have meant either finding another site or developing a treatment to eliminate dust.

The irritating properties of dust have been noted at all stations. It is common practice for personnel exposed to it to use protective clothing, particularly gloves and goggles. No major health problems have reportedly been evident yet.

Dust has also been identified as a factor in equipment reliability and maintenance. The erosive and corrosive properties of the ash have resulted in additional maintenance and in attempts to condition the ash for dust reduction.

3.4.2 Exothermic Effect. Without the exothermic effect, disposal of the waste would appear to be relatively simple. Ash could be loaded into a dump truck and sprayed

with water. The wetted ash could then be transported and dumped with no significant dust generation.

However, the exothermic reaction of the ash with water appears to be largely the reason for the ash being often transported in a dry form. Conditioning the ash with water before disposal results in a truckload of very hot, possibly steaming, material. Some care must be taken to avoid the temperature from exceeding 100°C in the process, because steam is formed then. There also appears to be the potential for the ash, so treated, to solidify in the truck before unloading. This operation, though controllable - with care - on a small scale, would require refinement for a continuous large-scale facility.

The potential for violent exothermic reactions has been noted in operations using a concrete mixer truck as a treatment/conveyance system. If too much ash is added to the water in the truck too quickly, the mixture boils, and is projected ("burps") out the mouth of the mixer. The associated temperature rise provides a lower limit for the ash-to-water ratio that can be used, and costs of excess water hauling provides the upper limit.

The hydration reaction must also be considered in the precautions taken by those who haul the ash dry. Trucks are covered and sealed, as much against water as against dust generation. Loading is also conducted in ways that minimize access of moisture to the ash until it is deposited at the disposal site.

3.4.3 Ash Solidification. Ash solidification is a consideration wherever ash may come in contact with water. It is an obvious consideration for those who condition ash or haul it wet. If the haul is too long, the ash may solidify in transit. Residues of ash do solidify in trucks and in conditioning conveyors. These residues have to be washed out promptly, or broken out like hardened concrete later.

Reactive ash may even solidify on contact with humid air. It is necessary to restrict moist air from contact with baghouses or conveyor systems during stoppages in summer weather.

By contrast, ash which has been conditioned with insufficient water may become so hot that it dries within a short time to re-form a dusty material. The potential for such material to solidify when re-wetted is not known.

3.4.4 Transport Equipment at Disposal Site. Wet-hauled ash, either conditioned in concrete-mixer trucks or conditioned in a mixer and hauled by dump truck, can be driven on a few days after dumping. Either can be moved with earth-moving equipment.

Evidently, dry-dumped ash eventually sets enough to permit vehicle movement as well. No operator reported problems with getting stuck. AFBC ash was compared favourably with wet PCF ash as a road base. Both PCF ash and FGD sludge are probably considerably more demanding on vehicles, because they have a lower potential for strength development. Compaction of the ash by the ash-hauling and -moving equipment contributes to strength development. The degree to which this occurs, however, is not known.

The effect of freeze-thaw cycles on solidified and compacted ash at U.S. sites has not been reported. In Canadian climates, experience would likely be different. Documentation on the effects of heat and rainfall is also lacking.

3.4.5 Leaching. To date, in most plants, leaching has been, operationally, less a concern than dust. Some ash disposal takes place at hazardous waste sites, some at municipal landfills, and some at dedicated ash disposal sites or at the plant site. Leaching potential has been a more significant design consideration at Summerside, which is a federal government facility. There, the combination of permeable soil and high precipitation necessitated consideration of leachate prevention in the disposal area design. Such disposal area design considerations are likely to apply throughout eastern Canada.

Whether leachate is likely to be primarily generated by percolation through bulk ash or through cracks and channels in monolithic sections is not known. Cracks and channels, possibly a result of thermal expansion effects from slaking, heating, or cooling, and changes in chemical composition in the aging ash at several sites have been observed.

3.4.6 Dimensional Changes. The potential for expansion or contraction of deposited ash may exist. Ash that is conditioned and becomes hot may expand because of the presence of steam in the solidifying matrix. Conditioned ash would also be expected to shrink on cooling from over 100°C to ambient temperature, especially if water evaporates as the ash cools. Climatic effects as well as changes in composition due to drying and wetting cycles would be expected to affect the dimensions of solidified ash. Finally, slow changes in mineral composition may be expected to take place over time and bring about changes in dimensions.

3.5 Other Ash Materials

The preceding list of potential problem areas must be considered in the context of current practice and knowledge. Problems have occurred with many other

materials and processes, and approaches to their resolutions have evolved and been implemented accordingly. Many of these properties have been considerably more intractable or demanding on resources than those of AFBC wastes. The problem of dust is common to ash-generating industries. AFBC dust is a very short-term irritant; other wastes, those containing high concentrations of heavy metal, for example, have long-term, cumulative effects. Similarly, the control of exothermic reactions has been developed in the lime industry, for its particular operational context. AFBC ash has neither the undesirable mechanical properties of FGD sludge nor the persistency of wastes from mineral extraction.

In fact, if an easily disposed waste should have the following properties:

- dustless,
- odourless,
- easily transported,
- no need for special treatment or containment,
- no need for covering,
- no-generation of toxic leachate,
- non-interactive with the landfill environment,
- good mechanical strength (can be driven on), and
- physically and chemically stable over the long term

- then very few wastes are characterized by them.

4 THERMODYNAMICS OF THE EXOTHERMIC REACTION OF CALCIUM OXIDE AND WATER

4.1 Introduction

Analysis of bubbling-bed AFBC ashes from limestone beds has consistently shown the presence of calcium oxide (CaO), formed by the calcination of limestone and not completely consumed by the "sulphur-absorption" reaction during combustion. Calcium oxide reacts exothermically with water. This exothermic reaction of ash with water has been demonstrated in the laboratory and observed in the field many times: temperatures beyond 150°C have been recorded. Laboratory and field experiences also demonstrate that temperatures above the boiling point of water are commonly reached when ash is sprayed or mixed with moderate amounts of water.

Although this release of heat has reportedly not been a crucial problem in small plant operations, to date, it has significantly influenced not only equipment selection but also handling and disposal practices because a potential exists for this reaction to occur during handling, transportation, and disposal as well as in the landfill. The potential energy release depends directly on both the quantity of the waste and its CaO content. In some cases, the quantity may be very large. Consideration of the chemistry and thermodynamics of the system can help to predict the results, when a large quantity of ash is to contact water over a short time.

4.2 Thermodynamic Properties

The thermodynamic properties of calcium oxide, water, and calcium hydroxide are as follows:

Compound	Heat of Formation at 25°C (298°K) (kcal/gram-mole) (ΔH_{298}) (36)	Entropy of Formation at 25°C (cal/°-mol) (ΔS_{298}) (36)	Free Energy of Formation at 25°C (kcal/gram-mole) (ΔF_{298}) (36)	Heat Capacity at 25°C (cal/°-mol) (Cp) (37)
Calcium oxide	-151.9	9.5	-144.40	10.0
Calcium hydroxide	-235.8	18.2	-214.33	20.83
Water (liquid)	-68.32	16.72	-56.69	18.0
(vapour)	-57.8	45.11	-54.64	8.64

Using these values, and the relationships

$$\Delta F = \Delta H = T\Delta S$$

$$\Delta F = -RT \ln K \text{ (van't Hoff equation)}$$

$$K = \frac{(Ca(OH)_2)}{(CaO)(H_2O)}$$

$$\Delta H = \Delta H_o + \int C_p dT$$

$$= \Delta H_o + \Delta\alpha T + 1/2\ \Delta\beta T^2 + 1/3\ \Delta\gamma T^3$$
(C_p is a function of temperature)

and $$\Delta F = \Delta H_o - \Delta\alpha T \ln T - 1/2\ \Delta\beta T^2 - 1/6\ \Delta\gamma T^3 + I\ T$$
(C_p is a function of temperature)

or $$\Delta F = \Delta H_o - C_p T \ln T + I\ T$$
(C_p is independent of temperature)

where:

ΔF	=	change in Gibbs free energy
ΔH	=	change in heat content
ΔS	=	change in entropy
T	=	temperature, K
K	=	rate constant
(x)	=	"concentration of x"
R	=	gas constant
ΔH_o	=	change in heat content at 0°K
C_p	=	heat capacity at 25°C
$\Delta\alpha'\beta'\gamma$	=	values for calculating changes of heat capacity at any temperature
I	=	constant

It can be shown that the reaction

$$CaO + H_2O \rightarrow Ca(OH)_2$$

goes substantially to completion at any temperature above freezing up to at least 400°C.

The reaction is accompanied by an energy release of 106 kJ/g·mole (15 580 cal/gram·mole) at 25°C. Such an energy release could, under certain conditions, cause temperature increases of hundreds of degrees to occur.

The relationships between composition, temperature, and pressure can be illustrated graphically (Figure 4-1). For purposes of illustration and computation only, it has been assumed that the other components of the ash do not contribute to the heat of reaction either positively or negatively and that they have an average heat capacity similar to that of calcium hydroxide. The relationship of the quantity of calcium oxide in

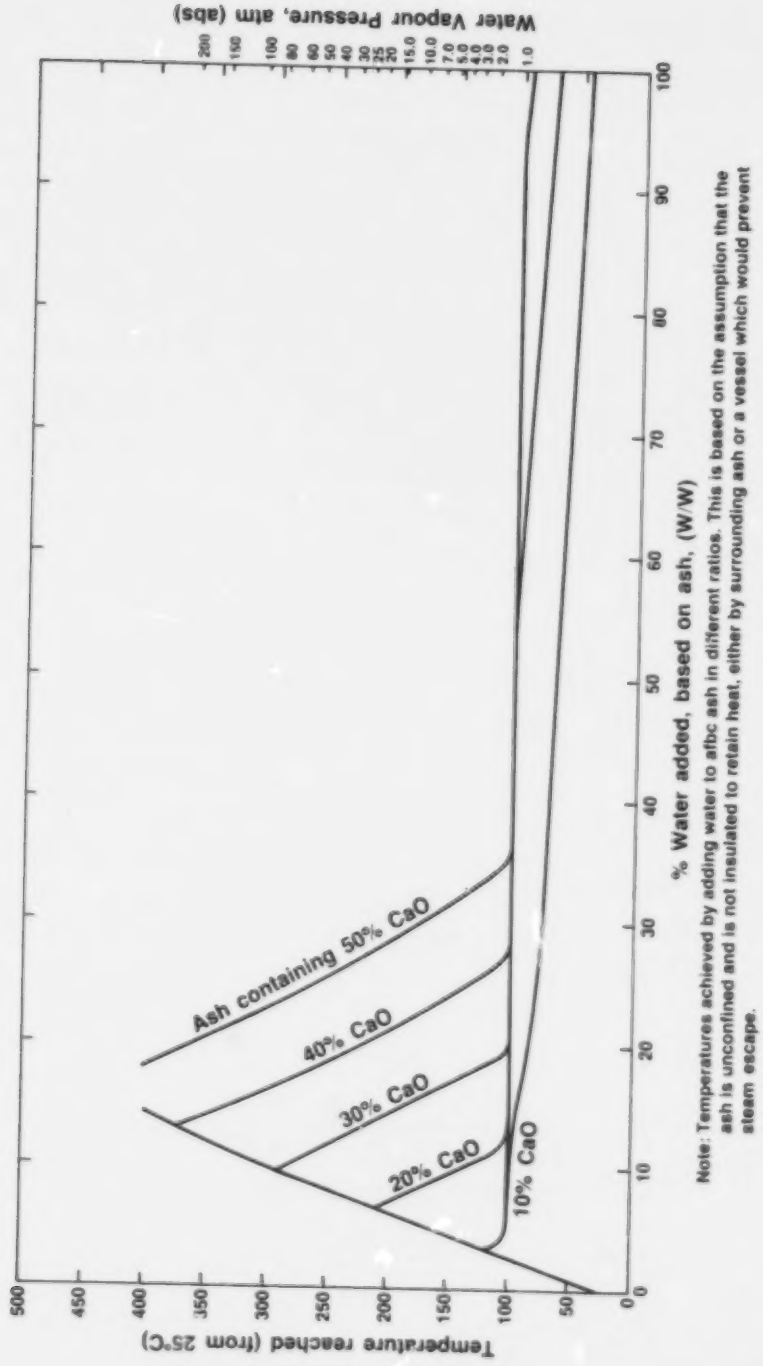


FIGURE 25 THEORETICAL PROJECTION OF WATER ADDITON vs. TEMPERATURE

the ash to such key process variables as sulphur content and ash content of the coal, and calcium-to-sulphur ratio is shown in Appendix B. According to these assumptions, the addition of less than about 2 percent of water based on total ash mass, would not raise the average temperatures of the ash-water mixture above 100°C. Also, an ash mass containing less than about 10 percent calcium oxide would not raise the temperature above 100°C.

The relationship illustrated corresponds with the laboratory experiences outlined in Section 2, Summary of Existing Published Knowledge. With ash containing 10 percent calcium oxide, the boiling point of water is exceeded only when 3 to 4 percent water is added, with a maximum of 120°C at about 3-1/2 percent water (the stoichiometric ratio of water to lime). Under these theoretical conditions, there would be very little uncombined water in the mixture, hence a pressure increase due to steam generation would not occur. At 20 percent lime, however, the boiling point of water would be exceeded when 3 to 12 percent water is added to the ash. The maximum temperature expected would be about 205°C with a stoichiometric ratio of water to lime, i.e., the addition of about 6 percent water. Above 6 percent, free water at temperatures above 100°C would exist. In a closed system, a pressure of several atmospheres could then result.

With ash of greater lime contents, the range of water addition rates posing a heat and pressure hazard widens:

- at 40 percent lime, for example, superheated steam can be expected for water additions of 13 to 27 percent;
- at 50 percent lime, superheated steam can be expected for water additions of 16 to 35 percent.

Between water addition of quantities of about 3 percent at the lower limit of these ranges, temperatures would still be high, but steam pressure would be absent.

These relationships indicate that a "fast reaction" composition range exists for lime waste and water mixtures. Estimates of the range of these "hazard windows" are based on several assumptions:

- The heat capacity of the ash is similar to that of calcium hydroxide. In fact, it may vary significantly, and this variation would affect the width of the hazardous water-to-lime ratio range.
- The calculations assume that the ash and water are well mixed. Unless ash is stirred into the water, this is unlikely to occur. In practice, there will be zones of a high

and of a low water-to-ash ratio in any mixer. Consequently local overheating and pressure buildup may occur even though the overall water-to-ash ratio is outside the hazard window.

- Heat release or absorbtion from other reactions is disregarded. Additional heat generated by hydration of anhydrite, a major constituent of the ash, to gypsum, or from reactions with silicates, has not been included.

The hazard window can be more precisely defined by establishing heat capacities and heats of hydration or mineral formation. However, the local overheating effect would remain an equipment-related factor that could best be resolved empirically, probably by allowing for a significant safety factor in determining the optimal rates of water addition.

4.3 Runaway Reaction Potential

4.3.1 General. It has been calculated and demonstrated in laboratory and field that temperatures above the boiling point of water are generated by reactions between ash and water. Some of the observed incidents include ruptures of the containment vessel and projectile discharge of the reactive mixture from vehicles or test equipment. It is not known whether these accidental reactions which "runaway" are the result of water-to-ash ratios of the wrong proportions or whether the heat buildup in the particular reaction mixtures caused an increase in the reaction rate with accompanying acceleration in temperature rise, steam generation, and internal pressure buildup.

The National Lime Association (37) has identified variables that affect the "quality of slaked hydrate" (calcium hydroxide solution or slurry), the product of the reaction of quicklime with water. They are:

a) Reactivity of the quicklime: this influences speed of slaking and temperature achieved in slaking;
b) Particle size: smaller particles hydrate faster;
c) Quantity of water: too much cools the mixture, too little causes overheating and/or poor mixing; therefore the quantity of water affects speed of slaking and temperature;
d) Temperature of water: reaction rate varies with temperature;
e) Distribution of water: good mixing produces more uniform slaking; and
f) Agitation: strong agitation results in faster reaction.

Since slurry is made by adding, under agitation, calcium oxide to water, mixing can be very good. Pastes are made by adding water to lime in a high-shear mixer, so that mixing is quite thorough, although the potential for heat transfer is limited. The implication is that contact with water (lime reactivity, mixing, quantity of water, particle size), and temperature (amount of water, temperature of water) are the determinants of reaction rate.

Quicklimes that exhibit a high reactivity require either more or cooler water to absorb the heat of reaction. Preferably the reaction mixture is kept below the boiling point of water. A total reaction duration of 5 to 10 minutes is considered desirable for lime-slaking.

In the slaking process, the reaction rate of less reactive quicklime can be accelerated by use of hot water, use of finer particle size lime, and agitation. These techniques applied to reactive lime can cause a reaction rate so rapid that "the lime and water literally explode on contact" (38). Also, if insufficient water is added, temperatures of up to 260°C may occur (38).

At the other extreme, use of water that is too cold apparently reduces the penetration of water into particles and results in a very slow or incomplete reaction.

In lime-slaking practice, process control leans toward adding lime to water in such proportions and at such a rate that the heat generated is absorbed by the heat capacity of the diluting water. No other control on the reaction rate is used. The proportions to be used are determined in advance from knowledge of the lime properties rather than by in-process adjustment.

4.3.2 Theories About Thermal or "Runaway" Reactions. The thermal explosion theory, as discussed by Gray and Lee (38), "is concerned with the competition between the heat generated in the exothermic reaction and the dissipative processes of conduction, convection and radiation by which it is removed from the zone of reaction". If the rate of heat loss is less than the rate of heat generation, the temperature rises and the rate of heat generation increases exponentially. Because the rate of heat loss is linear with temperature, the rates of reaction and temperature increase accelerates explosively. To identify the limiting equilibrium, Semenov's steady-state model (39) equates the rate of heat generation per unit time with the rate of heat loss to the surroundings as follows:

$$\frac{dq_1}{dt} = QVPA.e^{-\frac{(E)}{(RT)}} = \frac{dq_2}{dt} = XS\,(T-To)$$

where, dq_1/dt = rate of heat generation
dq_2/dt = rate of heat loss
Q = heat release per unit mass
V = volume of heat loss
p = density
A = constant
E = activation energy
R = gas constant
X = heat transfer coefficient
S = surface area
T = temperature
To = initial temperature

The quantity of heat dissipated depends generally on the surface area (heat exchange area) of the reactive mass. The quantity of heat produced depends on the reactive mass as a volume function. For a given reaction, then, heat dissipation varies with $(\text{mass})^{2/3}$; heat generation varies with mass. Under the same conditions, a larger mass would, therefore, favour runaway reactions more than a smaller mass.

This is significant because as FBC unit size increases, the rate of ash production increases. Many tons of ash may then be produced which require disposal rapidly in large dumps.

Implicit in this model are two assumptions:

a) All reactants necessary are present in the reactive mass.
b) The rate of the reaction is controllable by external heating or cooling. In general, this requires rapid mixing of the entire reactive mass.

These conditions do not precisely apply in conventional lime-slaking practice, because one reactant, lime, is added to the other in proportions that control the temperature and rate of reaction. Control by heat exchange is not practised. The process rate is adjusted by reactant proportions rather than by temperature control. A controlled slaking reaction is one in which the water-to-lime ratio is sufficient to cause all lime to be slaked, with enough excess water to absorb the heat released and maintain the reactive mixture at a desirable temperature.

The assumptions are even less applicable in the context of a dry AFBC ash dump. Water would be absent from the mass of the ash initially, and any fast reaction

would most likely be initiated only by large amounts of water coming into contact with the surface of the ash or by water channelling its way into the interior of the ash dump. Mixing would not occur, but heat transfer from the interior would be by conduction through the mass.

A runaway reaction in either case would be one resulting from a water-to-lime ratio that does not absorb the heat of reaction, but permits the temperature to rise above 100°C (e.g. concrete-mixer truck in Section 3.4.2), possibly accompanied by the generation of superheated steam. The steady-state model does not appear to be useful for describing the calcium oxide/water system under potential field conditions. This limitation is largely due to the lack of mixing. The reaction rates are too rapid to allow adjustment of conditions to permit an equilibrium. A behaviour model that does not require the assumptions discussed earlier would appear to be more suitable.

Another concept which was also examined in comparison to the ash/water system was that of a vapour explosion. This is the result of a rapid transfer of thermal energy. Occurrences have been demonstrated where molten metal comes in contact with a cool liquid, or when liquefied natural gas is released into water. The resulting explosions are the result of the very fast conversion of liquid to gas - fast enough that the sudden volume expansion produces a shock wave. In these cases a sudden event initiates the energy release, which is completed in a very short time, about 5 to 15 ms for a metal-water explosion (40). This contrasts with the "runaway" reaction model above, which is based on a relatively gradual acceleration in reaction rate once the reaction is past an equilibrium position, finally culminating in a "runaway" rate increase.

Several mechanisms have been suggested for the initiation of physical explosions in the molten metal-water system (41):

- On trapping water under molten metal, the water vaporizes rapidly, dispersing the metal into fine particles which rapidly transfer heat to the surrounding water.
- A ball of molten material begins to freeze on falling into water, trapping some water within fissures or pores. The ball shatters as the water in its interior vaporizes.
- A ball of molten metal is quenched in water. In the transition between film and nucleate boiling, boiling becomes violent, and large mixing forces are generated. These rupture the steam-metal interface, accelerating liquid water and metal into the interface region, which causes good contact and rapid energy exchange.

- Water is entrapped in falling metal drops, vaporizes and fragments the droplet with close water/metal contact and high energy transfer.
- The inertial forces on the falling metal drop exceed the forces of surface tension resulting in dispersion and rapid energy transfer.

Interestingly, the work available for a hot-metal/water system is maximized at a water-to-metal ratio of between 0.05 and 0.15 (40), with a rapid decline as the amount of water is increased. This is analogous to the situation for producing superheated steam with water and ash. In addition, the potential for explosion is reduced greatly, if the metal is dispersed into thin streams before contacting the water and if water-to-metal ratios of over 3 are used. Lime is also more safely handled under such circumstances.

The National Lime Institute (37) has referred to the potential, under certain conditions, "to obtain extremely rapid, almost instantaneous slaking so that the lime and water literally explode on contact". The potential for reaction speed of the order required for a steam explosion does not seem high, based on references to reaction completion in 5 to 10 minutes. However, the 5- to 10-min reaction time normally occurs under such controlled conditions that 100°C is not exceeded; i.e., with a large excess of either lime or water in the process at any time. The steam/metal explosion process is in fact similarly controllable by addition rate and metal/water contact characteristics, although it takes place at considerably higher temperatures and temperature differentials than the lime/water reaction.

4.3.3 Applicability to the Ash-Water System. The characteristics of the fast reactions involving ash of high CaO contents have not been well documented yet. Violent reactions have been observed in concrete-mixer trucks and in the laboratory. Whether these are due to pressure buildup in a confined reaction space or to a sudden pressure rise due to vaporization of water in contact with hot slaked ash is not yet known. A suggested sequence resulting in the possibility of the occurrence of a sudden pressure rise is as follows:

1. A quantity of dry ash is deposited for storage or disposal.
2. A large quantity of water, say 20 percent of the ash mass, comes into contact with the ash through channelling into the interior.
3. The calcium oxide of the ash reacts with a portion of the water and vaporizes part of the rest.

4. The steam produced forces heated water into contact with unreacted portions of the lime.
5. Further reaction, vaporization of water, and steam contact with unreacted lime occurs, this time faster because of the increased reaction temperature.

The potential energy release from large ash masses could be considerable since the energy available from any 1 kg of calcium oxide is significant.

However, in the "runaway" heat release model, close contact between reactants is assumed as an initial condition. In the vapour explosion model, close contact is itself a cause of the violent reaction. By comparison, close contact in the hazard window region of the ash/water system appears to lead to faster release over a period of several minutes. This behaviour follows neither of the two simple models of rapid energy release and indicates a more complex sequential pattern which includes characteristics similar to some in the less complex models. All this suggests that there is a potential for problem reactions (e.g., steam formation, rapid cementing, rapid expansion, violent ejection of material) to develop under a variety of conditions. Furthermore, the optimum water-to-ash ratios for economical treatment and disposal fall within the hazard window region.

By implication, this means that a continuous potential hazard to personnel and property exists during handling of this ash. The potential hazard will depend on the margins of tolerance incorporated into future designs of handling systems.

The potential for problems in the case of landfilled unslaked ash appears less likely but has been even less completely assessed. A unit of 100 to 200 MW, running on 6 percent sulphur coal and a calcium-to-sulphur ratio of 2:1, for example, could produce ash quantities of the order of 180 000 to 363 000 tonnes of ash a year, containing at least 20 percent lime. Higher calcium-to-sulphur ratios, up to 3:1, are more likely with current bubbling-bed designs and would result in somewhat greater ash quantities and proportionately higher calcium oxide contents. The stability of such masses in the presence of moisture in the long term has not been thoroughly addressed in any studies to date.

5 WASTE DISPOSAL

5.1 General

Evaluation of disposal options of ash with high CaO content should begin by considering that present technology has not yet developed to the stage where simple, problem-free handling and transport of material with a high CaO content to the disposal site can always be guaranteed. The appropriateness of current disposal techniques is even less clear, and future disposal needs for very large quantities are even less well defined.

Standard techniques and equipment for conventional waste disposal may not be directly transferable to AFBC waste with high CaO content because of its environmental, chemical, or handling properties. A variety of systems suited for municipal solid waste or PCF wastes appears to have some severe drawbacks when applied directly to AFBC waste disposal.

From a disposal standpoint, the identified characteristic of AFBC ash of most interest is its calcium oxide content. This distinguishes it from conventional solid wastes, and particularly from PCF ash, in that:

- the dry ash becomes very reactive (unstable) on contact with water;
- the ash releases considerable heat on contact with water;
- the ash appears capable of absorbing considerable quantities of water;
- the ash solidifies in certain circumstances following contact with water;
- physical properties of ash may vary considerably, depending on hydration state and reaction conditions;
- leachate or runoff from the ash can be expected to be strongly alkaline until sufficient atmospheric contact and CO_2 uptake occur.

Like other ash, it can be:

- dusty initially;
- generated in large quantities;
- conspicuous in its handling and disposal.

All these factors must be considered when selecting a disposal method to optimize the overall effect.

5.2 Environmental and Handling Constraints

5.2.1 Reaction With Water. The reactivity of ash containing a significant amount of lime with water appears to impose limitations on the selection of treatment and disposal

methods. If all of the ash is treated with enough water to eliminate dusting during handling, the heat generated may make handling difficult: the ash and hence the disposal vehicles become dangerously hot; steam is ejected and hot ash spattered. If deposited on an unprotected synthetic liner while still hot, the liner could be destroyed by the heat. The ash may also dry out because of the heat of reaction and regain its dustiness at the disposal site, or it may, if overwetted or unreactive, be sludge-like and difficult to handle. In addition, the initial and subsequent reactions may result in a concrete-like product, setting too quickly in trucks or mixing equipment during treatment or transport and therefore necessitating labour-intensive manual removal. If the right amount of water is added, the ash can be driven on shortly after deposition. If too much or too little water is added, its movement by bulldozers only may be practical. The amount of water required for good handling and transport properties is quite close to the amount that causes significant heating, possibly resulting in forceful steam and material ejection as well as swelling.

If the ash is transported dry, it may dust heavily at the disposal site, requiring all personnel in the area to use lung and skin protection. This is not generally acceptable where winds may carry dust off-site, especially to populated areas. It will also react with any available moisture in the disposal site, leading to as yet unpredictable short- and long-term results.

Finally, if the ash is treated with sufficient water to limit the temperature rise, the ash must be handled like a paste or slurry. This imposes two cost increases. First, the transportation and disposal costs become greater because significantly more mass must be hauled and deposited. Second, wastewater or leachate can be generated as the excess water drains from the deposited ash. This wastewater may then add significantly to the wastewater treatment costs if the volume is large.

5.2.2 Scale. The current disposal options for the ash depend largely on the scale or rate at which the ash is produced, and on the scale on which equipment is commercially available. Relatively small amounts of ash, such as those produced in pilot facilities, can be treated on an ad hoc basis. The ash can be water-sprayed or aerated, and conveyed to the municipal disposal site in drums. If treated by a wet process, adjusting the pH of the wastewater with acid and draining it to surface water or sewage plant may be feasible. Direct scale-up of these approaches to large industrial or utility volumes may not be practical. Handling wastes on these scales requires a designed disposal system, beginning with ash treatment at the generation site and continuing with provisions based on ash and

leachate composition at the final, selected-by-design disposal site. 1000 L of waste a day may be handled by municipal treatment systems; 10×10^6 L is less amenable to that treatment.

5.3 Options

5.3.1 General. To date a wide variety of wet and dry handling techniques have been tried and used in the field at small facilities. The techniques used depend on the ash generation and disposal site characteristics. These techniques have initially been adopted from PCF or municipal waste practices, with modifications derived from other technologies, such as those used in the lime industry. The modifications appear to have been remedial rather than planned in advance. The factors considered in selecting a disposal technique include the type of disposal site available, quantities of ash, distance from ash generation point to disposal site, regulatory constraints, and soil and ash characteristics. The handling approaches may be grouped under "wet handling" or "dry handling" depending on where the treated waste fits in the range of properties from slurry to dry powder. Advantages and disadvantages must be weighed in terms of the requirements of each unit.

5.3.2 Wet Handling. Disposal of ash by dumping or conveying it into a large water lagoon is the simplest form of wet disposal. It has been practised in various forms with PCF ash. For AFBC ash with a high CaO content, the lagoon becomes a lime-slaking vessel.

The advantages are:

- the heat released in the slaking process is controlled;
- dust is well controlled at the disposal site;
- the plant can handle the ash dry;
- technology is readily available;
- recirculating ("closed") system water usage designs may be used.

The disadvantages are:

- a dedicated slaking pond is required;
- alkaline leachates must be controlled by liners or other means;
- water use is high;
- wastewater treatment cost or recirculating water treatment cost may be high;
- unless it is very large, the lagoon ultimately needs to be dredged and the solids disposed of. Lagooning is not the final stage of disposal;
- local regulations may not permit lagooning,

- environmental impacts of a lagoon failure may be severe;
- dusting problems at the generation site need solving;
- low moisture uptake conditions must be maintained during transport;
- suitable for utility-scale operations, where the cost of the lagoon system can be justified;
- control of the rate of ash feed to the water is necessary to avoid local overheating and the hazards associated with it.

Variations in wet handling approaches are in use in both ash disposal and other industries:

- ash may be handled by pneumatic injection through a pipe under water;
- a jet mixer or eductor may be used to mix lime and water in a 1:2 ratio (weight) and project it into a lagoon. Currently available equipment can handle 18 tonnes/h.

Although the lagoon treatment is straightforward, the conditions required for its use and the need for further treatment of dredged material and wastewater reduces its attractiveness. Processes to handle the wet waste at higher concentrations become more attractive because water use, wastewater production, and containment needs are reduced. Processes with such characteristics may be adopted from lime-slaking practice. Lime is slaked either in batch or in continuous processes to produce either a slurry of 10 to 30 percent solids or a paste of about 40 percent solids. Slurry is generally produced by the simultaneous addition of controlled amounts of lime and water into a mixing tank. Numerous designs are available. A consistency of paste is obtained by using a pug mill system: the slaking compartment is trough-shaped, with two sets of paddles mounted on counter-rotating shafts to provide mixing. Water and lime are fed concurrently into the mixer; its contents are maintained near boiling by the heat of reaction. The lime-to-water ratio is controlled by a torque-activated water valve. The process is fast, with residence times of 5 to 10 minutes. Capacities of commercial units are not great, however; units with capacities of up to 3.5 tonnes/h are currently available. Development or modification could adapt the equipment better for ash treatment. This process is very similar to that used at the Shawnee bubbling AFBC unit, and ash handled this way could be nearly free of dust and wastewater. The ash would, however, be hot, corrosive, and prone to solidification or re-drying, or both, after deposition. If it solidifies while hot, cracking would be likely to occur on cooling, with resultant channelling which, in turn, promotes the production of leachates.

Use of a concrete-mixer truck is also practical, within limits. The mixer trucks perform the same functions as those of a stationary paste slaker, except that they are carried out en route to the disposal site. As in the paste-slaking operation, a considerable amount of heat evolves and the mixture may solidify, if the proportions are not correct. Loss of water through evaporation decreases, however, because the material in a concrete-mixer truck is more completely enclosed than in a paste slaker. Balanced against these factors is the high cost/tonne-km of using a concrete-mixer truck as transportation, its labour-intensivity, and the imprecise control of the water-to-ash ratio in a mixer. With both concrete-mixers trucks and paste slakers, outdoor operation in winter could be a problem.

5.3.3 Dry Handling. Transport of dry ash by truck to a landfill disposal site is, superficially, the simplest of all possible disposal methods. The advantages are:

- minimum water usage;
- no risk of wastewater production, and therefore, no need for wastewater treatment:
- minimum tonnage hauled;
- ash is conveyed at ambient temperatures;
- the ash, if it remains dry, is stable in transport; and
- vehicle requirements are simple: a covered dump truck or a tank truck.

There may be other advantages as well, although data are sparse. For example, dry ash may absorb water continuously for a considerable period, until all the lime has reacted and all the physical absorption capacity of the fines is saturated. This would limit leachate formation, at least in the short-term. The long-term behaviour of ash is not known yet. However, the potential for the level of hazard exhibited by the waste seems to decrease with time because of the gradual moisture and carbon dioxide uptake from the atmosphere.

The problems associated with dry ash are:

- dust at plant and the disposal site;
- material handling systems must be kept moisture-free;
- ash cannot be allowed to become wet during transit;
- spraying of deposited ash to reduce dusting may be unsatisfactory in winter and labour-intensive in summer;
- massive deposits of dry ash on a utility scale could remain unreacted and possibly a hazard for a long time.

5.3.4 Other Approaches. Other potential approaches to handling "nearly dry" or stabilized solid-phase ashes include land disposal, conditioning of the waste, and processing and recycling of bed material.

Land disposal. This is a technique similar to landfarming. A tractor would disc furrows into the soil at the site, the dry ash is injected into the furrows, which would then be covered in the harrowing process. The ash would absorb soil moisture and become mixed with soil during ensuing passes. Use of fly ash to stabilize oily waste landfarms has also been reported. At this time, long-term effects on soil are not known. The amounts that can be disposed of in most instances would be small, possibly only a few tonnes. Winter application would be impractical in most of Canada.

Conditioning of the waste. By using hot flue gas as a source of carbon dioxide and water to condition the waste, both exothermicity and alkalinity would be reduced, possibly resulting in savings in leachate control and treatment at the final disposal site. The concept does not appear to have been tested extensively in field or laboratory work yet.

Processing and recycling of bed material. To increase utilization of calcium in sulphur capture, bed material could be processed and recycled. Some AFBC users have expressed interest in this concept as a means of reducing the costs of both limestone and disposal. However, anticipated calcium utilization modifications in newer AFB combustor designs, such as circulating units, are expected to improve calcium-to-sulphur ratios on the larger units so that the cost/benefit ratios for reprocessing would be most favourable.

5.3.5 Conditioning/Dry Hauling. The drum conditioning unit is on the borderline between wet and dry handling, depending on the water-to-ash ratio used. As practised, an ash-water mixture at 100°C is allowed to cool and solidify before being transported to a disposal site. There the ash would be left to continue to solidify before being progressively covered by more ash. It is likely to continue reacting while being transported. Behaviour in rain is not known; the effect of winter temperatures on solidification is not known. Equipment availability is still limited.

5.3.6 Other Considerations. The practice of ash conditioning results in changes to the chemical characteristics, ash handling and disposal properties. Increases in water content affect some properties favourably, others adversely. Water content affects these relationships:

- soil strength,
- dust,
- "stickiness" - ease of handling,
- temperature reached,
- solidification potential,
- transport cost, and
- wastewater treatment needs.

How they are qualitatively affected is shown in Figures 26 and 27. The potential usefulness of various techniques evidently vary with the scale of the operation. This is shown in Figure 28. This figure is not intended to include all current practices, because some may not be suitable in any foreseeable Canadian context.

In summary, deposition of dry ash in a landfill site in large quantities may pose some environmental and safety problems which require further examination of both ash behaviour in landfills and landfill design concepts.

Wet handling of ash (lagoons) is mechanically possible but may pose some treatment or equipment problems, or both.

Conditioning ash with water and handling it as a partially reacted solid has environmental advantages, but at present, practical means for doing this on a large scale have not been fully developed. Physical problems, such as the fast heat of reaction and the potential for solidification, have yet to be resolved. Also the ash/water reaction characteristics requires much more attention than it has received to date before an optimized waste management system can be developed.

TABLE 6 TREATMENT NEEDS OF AFBC UNITS OF DIFFERENT SIZE

Laboratory	Summerside/ Industrial Size	10-100 MW	Large Utility (100 + MW)
Small	Scale		Large
• Neutralize or slake manually, • Drum and send to municipal landfill	• Adopt equipment/ techniques from other industries, • Cement truck, • Condition in pugmill, • Dry disposal with spraying or landfill.	• As yet untried techniques or scale-up of existing techniques.	• Wet-dispose using PCF techniques or lime techniques, • Condition/dry dispose using as-yet untried concepts, • Scale-up of conditioning techniques.

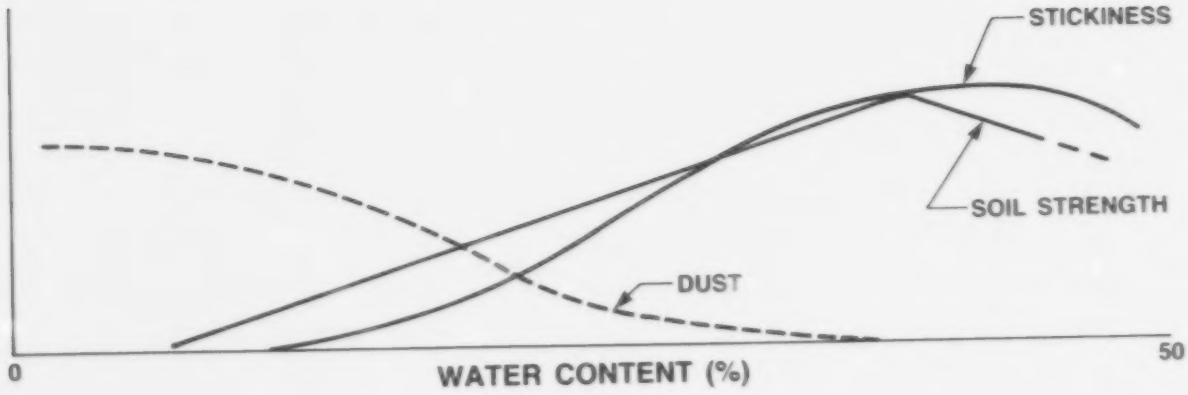


FIGURE 26 EFFECTS OF WATER CONTENT IN ASH ON STICKINESS, DUST, AND SOIL STRENGTH

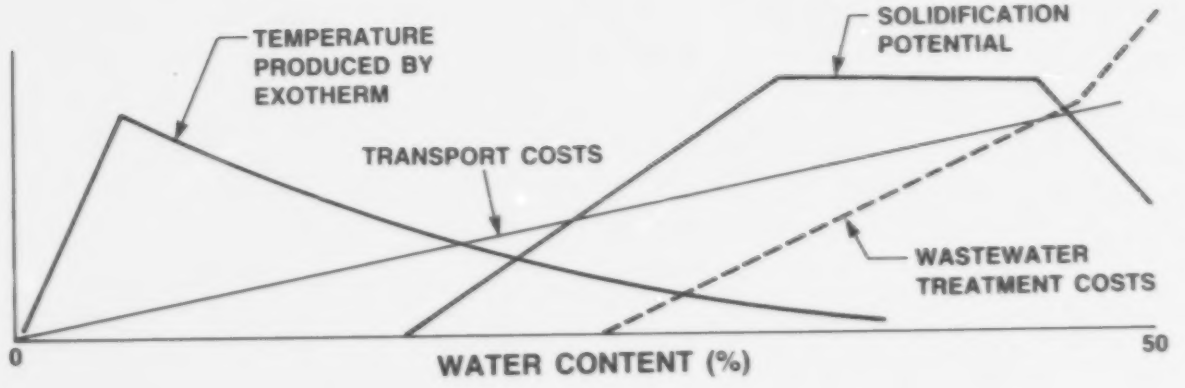


FIGURE 27 EFFECTS OF WATER CONTENT IN ASH ON TEMPERATURE PRODUCED, SOLIDIFICATION POTENTIAL, AND COSTS OF TRANSPORT AND WASTEWATER TREATMENT

6 SUMMARY

6.1 General

For a variety of practical, economic, and environmental reasons, AFBC technology is now developing rapidly from pilot- through medium- to large-scale power utility applications. Several coal-fuelled units of 100 MWe and larger and of various new designs are now under construction in North America and the construction of more units is under active consideration. Environmentally, AFBC permits the combustion of high-sulphur coals with simple, effective control of the SO_x and NO_x emissions which are major contributors to acid rain.

As with other pollutant-capture technologies, the rate of waste accumulation at the generation site increases. At this stage of FBC technology development, the management and environmentally safe disposal technologies for these particular wastes are less advanced than the combustion technology. As the technology continues to scale up, it appears that waste management and disposal problems will continue to be encountered until waste management techniques that take the reaction characteristics and the quantities of the wastes into account are developed.

At this time, management practices for the FBC wastes generated in smaller units appear to have been borrowed largely from practices developed and optimized for other waste materials. However, AFBC wastes with high lime content, particularly those wastes from high-sulphur coal in limestone bubbling-bed combustion where significant stoichometric excess of calcium, (relative to sulphur) are required, possess some unique physical and chemical characteristics. To date, these unique characteristics have not been widely recognized and, when problems have been encountered in smaller units, they have been dealt with by various means on a situation-specific basis. While these methods may be adequate for small facilities, they may neither be appropriate nor acceptable for large-scale requirements. The experiences with small operations regarding their wastes and the techniques of disposal derived from them correspond to results from laboratory studies for waste characterization. They indicate unique waste reaction characteristics. Unless more attention is paid to these characteristics, waste management problems may become more significant as waste quantities generated on individual sites increase.

The component of the waste mixture that appears to be the most immediate source of unresolved problems is unslaked crystalline calcium oxide ("lime", "quicklime" or "CaO". AFBC wastes contain a variable mixture of components which can influence the

calcium oxide reaction significantly. The calcium oxide content of the waste, however, depends mainly on the stoichiometric excess of calcium carbonate required to control sulphur emissions satisfactorily (see Appendix B).

Calcium oxide has been produced in lime kilns and used for a number of well known industrial applications for many years. It is highly alkaline, and its reaction with water is exothermic and rapid. It can be classified as a Class 8 (corrosive) hazardous substance under the Transportation of Dangerous Goods Regulations (42) or as a reactive waste, a subclassification of "hazardous waste", under the 1985 amendment (43) of Ontario Regulation 309. The intermediate and final products of calcium oxide and of AFBC waste reactions with water have quite different characteristics.

The lime manufacturing industry and the users of lime have developed safe methods for controlling calcium oxide slaking and heat release rates as well as safe methods for production, handling, and use. These methods have evolved for particular applications and involve controlling the quantities or the mixing rates, or both, of relatively small quantities of material. Such methods and equipment are not entirely appropriate for very large quantities of AFBC wastes.

From the perspective of environmental protection, the methods and economic aspects of on-site waste management may appear to be of secondary interest as long as the problems also remain on-site. Of more direct, immediate concern is the potential for the escape of wastes as dust or in waste waters, for example, beyond the station boundary. However, the concerns about utility and environmental protection coincide, if costs for safe handling and safe disposal begin to hinder the acceptance of technologies, such as AFBC, as a feasible means to reduce SO_x and NO_x emissions significantly. In this respect, the greatest benefits to environmental protection concerns may arise from the development of environmentally sound solutions to two unusual properties of AFBC residue: its exothermic and violent reaction potential and its strength development potential. The exothermicity is of interest to environmental protection in that, with present knowledge, it may limit the ways of disposing of the unslaked residue safely. A possible result is that the "safe" disposal route chosen may be less than environmentally optimal because the exothermic and reactive nature of the waste affects all waste management options.

The solidification potential of the residue also imposes limits on how the residue may be reacted. It is prone to solidify within a certain (variable) range of the water-to-ash ratios, and within a certain (variable) time. Conditioning and transport

practices can be influenced by this solidification potential. Following deposition, the interval until traffic over the waste is practical also depends on the setting or strength development rate of the waste.

6.2 Recommendations

A number of potential waste management and disposal problems for bubbling AFBC residues with a high calicum oxide content have been identified. As with any developing technology, solutions to these problems can result from the elimination of the source or development of appropriate remedial measures or both. In this case it is likely that some of the problems associated with the significant lime content of these residues will eventually be reduced by process configuration and operational control improvements aimed at reducing the residual lime content. For the remainder, additional investigations to clarify the characteristics and extent of the problems, followed by the development of practical solutions, are required. The areas of present concern with AFBC wastes containing much calcium oxide are classified as:

- Environmental/Operational,
- Environmental, and
- Operational.

Recommendations for further investigations in each of these categories follow.

6.2.1 Environmental/Operational Study Recommendations.

Reaction potential. It has been demonstrated that, under some conditions, a rapidly, strongly exothermic and potentially violent reaction is possible. The conditions in which water contact with the ash will produce this undesirable reaction require further examination to permit development of waste management systems which take these conditions into account with sufficient safety margins.

Gaps in the reactivity information include:

- composition range susceptible to this reaction;
- factors affecting reaction rate;
    - exposure to moisture
    - exposure to carbon dioxide in air
    - temperature;
- hazardous ratios of water to ash; and
- effects of mixing efficiency.

The work should be conducted initially in a laboratory. When the hazardous conditions have been defined, demonstrations using 20 kg to 1 tonne should be done to assess the effects. The development of simple test protocols will be required. Use of production ash, possibly augmented with calcium oxide to simulate ash with higher lime content, is a suggested alternative.

Conditioning. Treating ash with water prior to disposal may be desirable to reduce:

- reactivity or dustiness of the ash,
- damaging effects of the heat of reaction from the ash on liners, and
- other potentially hazardous conditions.

At this time, such conditioning is carried out empirically and proves marginally satisfactory for small units, but the development and evaluation of larger conditioning systems for units of utility scale is also needed.

Optimally, a conditioning operation would produce an ash that is not unmanageably hot and that will not solidify en route to the disposal site, but which will eventually solidify to a stable mass after dumping.

If the ash is to be slaked and conveyed in a solid form, conditioning with too little water may leave the ash dusty, whereas too much water may liquify it. Between these extremes, some quantity of water may result in very high temperatures, ejection of hot ash, or a steam explosion. Similarly, if ash is to be transported as a fluid, too little water may produce a hazard through overheating, whereas too much water may mean excessive transportation and wastewater treatment costs.

A rapid, simple test to indicate how much water is optimal in the conditioning process should be developed. An investigation into the water-ash reaction characteristics should include the determination of:

- ash-to-water ratio to produce
  - dust-free ash,
  - paste-like ash,
  - pumpable ash,
  - unacceptably high temperature or pressure;
- bed-to-fly ash ratio, and how it affects the reaction with water;
- reaction speed at different water contents;
- solidification rate at different water contents; and
- effect of combustion conditions on ash conditioning.

Strength development. It is more convenient to dispose of ash that can support vehicular traffic within a reasonable time after deposition. Although some work has been done from the standpoint of development of structural engineering properties, it has not been particularly applicable to conditions associated with disposal practices.

The rate at which strength develops in ash can be expected to depend upon:

- bed-to-fly ash ratio and chemical composition,
- conditioning (water, air exposure history),
- compaction history,
- exposure to precipitation,
- freeze-thaw cycling, and
- aging before and after compacting.

These variables are similar to those expected to affect permeability. Quantification of these effects will facilitate selection of the most practical treatment regimes and disposal site designs.

6.2.2 Environmental Study Recommendations.

Permeability. The thrust of ash permeability work to date has been toward identifying properties of as-deposited ash. The permeability of ash as a function of the water-to-ash ratio and physical compaction has not been addressed. It is, however, reasonable to expect that conditioning and compacting will be used in the disposal of ash.

Tests should be conducted, considering the implications and effect of:

- different ratios of bed and fly ash;
- compacted and uncompacted ash (using a compacting effect similar to earth-moving and hauling equipment traffic);
- ash conditioned to different moisture contents; and
- aged and fresh material.

The information derived from this work identifies the effects of the ash history both on quantities and physical/chemical properties of leachate. With this information, ash handling, processing, and disposal practices can be selected for optimum disposal effectiveness.

Laboratory-scale tests should constitute the first phase. Ash that has been stored under moisture-free conditions should be treated under various air and water exposure regimes, then compacted in columns of appropriate size to a range of densities

similar to those obtained in field operations. Aging conditions between steps could be varied to simulate possible conditions of disposal such as sequences of rainfall events. Such studies should be conducted to encompass the expected field condition ranges and over laboratory-test ranges to provide comparability with permeability tests conducted in previous works. To do this, a reasonably precise measurement and analysis protocol should be produced and followed.

Liner effects. If AFBC residue is to be landfilled, containment of infiltrated precipitation becomes a priority. The leachate can be expected to be of high pH, at least initially. This requires liners made of alkali-resistant materials. Synthetic materials such as high-density polyethylene (hdpe) or Hypalon are expected to be resistant to such solutions. It is still not known whether synthetic or clay liners will endure long exposure, or whether treated clays offer a long-term advantage.

Exposure tests have been performed (1) on a variety of polymers. All showed some resistance to the solutions, and a gradual decrease in strength-related properties. However, other polymers; for example, hdpe, have to be evaluated. It is also possible that clay liners may be more effective for long-term containment than synthetic liners. No information on work characterizing their behaviour over the long term; e.g., 20 years, under such conditions is available yet. Data needed include the effects of high pH and precipitating calcium species on chemical and dimensional stability of clay and other soil materials.

The results of this work would indicate the most technically and economically satisfactory way of isolating the ash from the environment.

Leaching chemistry. The composition of leachate can be expected to vary with several factors, including:

- coal characteristics,
- limestone characteristics,
- calcium-to-sulphur ratio and CaO content,
- recycle ration,
- age/aeration/moisture history of ash,
- native soil in contact with ash,
- degree of compaction of ash/cover material,
- bed-to-fly ash ratio, and
- degree and manner of slaking.

The effects of these factors on such parameters as concentrations of chemical species, redox potential, pH, and effects of carbon dioxide exposure on the leachate and leaching process, must be described by the procedure. Development and verification of a test protocol to permit a realistic prediction of leaching behaviour is necessary. It must be determined, for instance, whether a water-ash mixing batch technique, open or closed, or a column-type test produces more useful results.

Knowing the relationship between leachate chemistry and ash parameters will enable optimal selection of ash and leachate treatment regimes.

Leachate treatability. After toxic properties of the leachate have been identified, leachate treatment options suitable for various site conditions will be required. These may include simple lagooning, neutralization and precipitation, or some form of recycling. It is anticipated that leachate treatment selection would be quite site-specific.

An effective method of leachate treatment, one embodying a significant safety factor, must be able to accommodate a range of variations, among them that of leachate composition. This would best be accomplished using, initially, standard waste-water treatment approaches in the laboratory.

Plowing into soil. It is well known that calcium oxide can be plowed into soil, to reduce moisture, increase stability, and provide calcium for plant growth. Testing a similar process as an ash disposal method would indicate whether such a low-technology, low-capital-cost approach would be effective for waste quantities generated by smaller bubbling FBC plants. It is not known whether continued application of ash to soil will result in a continuingly friable soil material, or whether the soil will progressively harden and become rock-like. It has been shown that ash, when wetted and compacted, becomes, superficially, almost concrete-like. But it has also been shown that unconsolidated ash remains crumbly, and that compacted ash deteriorates under some weathering and freeze-thaw conditions. It appears that some ash could be used in this way, however, and an upper limit to the quantity should be determined.

A test program, incorporating small proportions of ash in loose soil, would serve to answer these questions. After an aging period, the process should be repeated. The feasible ash loading per hectare before the soil-ash mixture becomes unworkable can be identified through repeated applications. Leachate and runoff studies would also be required.

To do this, a small proportion of dry ash can be deposited into plowed furrows, and then covered with soil. Subsequently, the area would be harrowed and have more ash

injected in the cross-direction. The process would be repeated until the system is demonstrated to be either practical or impractical. Work on a smaller scale is unlikely to be informative.

Dust emissions. AFBC ash is unlike PCF ash in its effect on the environment. AFBC ash is reactive and corrosive, and may impart high alkalinity to waters and surfaces that it contacts. At this time, the characteristics of the fractions of the ash emitted as fugitive dust are not known. These fractions should be identified and their composition and potential effect on the environment characterized. The objective is to determine the characteristics of emissions produced in low-temperature, high-alkalinity conditions, compared to PCF conditions. In this way, significant differences between AFBC and PCF emissions can be identified. Both trace organic and inorganic emissions are of interest.

6.2.3 Operational Study Recommendations.

Seasonal effects on strength development. Ash has been shown to develop enough strength to permit traffic over it at a disposal site; however, this has been demonstrated only over a short time period in a climate more temperate than Canada's.

To design a disposal site capable of handling disposal vehicular traffic over the ash requires information on:

- strength development in fresh and aged ash at various ambient temperatures;
- effect of traffic on strength development at various temperatures;
- effect of freeze-thaw cycles on the rates of strength development and deterioration under expected traffic conditions; and
- effect of heavy precipitation and standing water on strength development and deterioration.

The work will determine whether special precautions are required to stabilize the ash before driving on it in heavy precipitation or at low temperature. The landfill can then be designed and operated accordingly.

Effects of Dust. AFBC ash dusts are unlike PCF dusts in several important respects that may affect utility operations. The dust is reactive and corrosive, and it is not known whether this will cause health problems among workers during either long- or short-term exposure. Analysis of airborne fractions of the ash would identify the constituents likely to cause problems. Because of its reactive nature, it may also affect equipment wear in a plant.

Equipment failure due to erosion, corrosion, and cementitious reactions have been widely reported. In this case, the compilation of composition data is less important

than that of remediation data. Measures adopted by industry to prevent equipment-related failures should be identified and screened for possible applicability to demonstration- and full-scale units.

Dust composition should be characterized both chemically and by particle distribution. The composition of respirable material should be emphasized. This will require either classification of waste to simulate dust generation, or preferably actual in-plant sampling. If the composition suggests possible health effects, animal or mutagenicity tests should be considered.

Information to identify areas of maintenance problems, should be collected through a survey/visit program of significant users. Telephone surveys do not, in general, acquire nearly the same quality and amount of data that a visit does. In this case, establishing a large list of contacts at operating AFBC units (operating at high required availability), rather than demonstration units, is a first priority , so that information about the effect of their pragmatic solutions on other aspects of AFBC operation, such as environmental acceptability, can be gathered.

Swelling. Swelling of this material when wet - especially if it hardens as well - could cause major damage to equipment, such as the vehicles transporting it, and increase landfilling costs. Variations with swelling have been noted in the laboratory and the field, but not quantified to date.

The information needed includes:

- ash compositions susceptible to swelling,
- effect of ash aging or conditioning,
- relationship of swelling with time and water content, and
- effect on swelling from soils mixed with ash.

This data will enable ash conditioning and transportation without risk of damage to equipment. Control of swelling, when in place, will minimize damage to landfill liners and reduce water infiltration into the emplaced mass, thus reducing the leachate potential.

6.2.4 Other Study Considerations.

Identify real and social costs of disposal. Whereas landfilling charges have traditionally been only a few dollars per tonne, the effects of landfilling have often been environmental contamination and, in some cases, costly remediation procedures. The relative total costs and benefits of disposal methods should, ideally, be assessed before a

decision about disposal is made. Each disposal option should be costed comprehensively in both economic terms and environmental/social terms. With a new technology, such as FBC, where there are still too many unknowns and the technology is still evolving, a comprehensive and accurate analysis based on experience will not be achieved for a number of years. Similarly, disposal costs should also be weighed against the benefits from air emissions controls of the technology. However, the accumulation of the necessary information and on-going refinement of estimates should now be initiated in a comprehensive manner with these long-term objectives in mind.

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APPENDIX A
AFBC FACILITIES IN NORTH AMERICA OPERATING ON COAL (32)

Company	Location	Start-up Date	Boiler Capacity (lb/hr) x 1000
1. California Portland Cement Co.	Colton, CA	3/85	190
2. Tennessee Valley Authority	Paducah, KY	6/82	170
3. Quaker State Oil Refining Corp.	Newell, W. VA	2/85	120
4. Midwest Solvents Co.	Pekin, IL	4/84	120
5. Georgetown University	Washington, DC	7/79	100
6. Sohio Oil Corp.	Lima, OH	10/84	70
7. Iowa Beef Processors Inc.	Amarillo, TX	9/82	70
8. Idaho National Engineering Lab	Idaho Falls, ID	3/84	68
9. Steam Heat Authority	Wilkes-Barre, PA	2/84	60
10. Kentucky Agricultural Energy Corp.	Franklin, KY	10/82	60
11. Gulf Oil & Exploration Co.	Bakersfield, CA	/83	50
12. Central Soya Co.	Marion, OH	4/79	40
13. Canadian Dept. of Defence	Summerside, P.E.I.	12/82	40
14. Babcock & Wilcox Co.	Alliance, OH	5/78	20
15. Texas Tar Sands Ltd.	Maverick County, TX	/82	50
16. Campbell Soup Co.	Maxton, NC	/82	50
17. Campbell Soup Co.	Napoleon, OH	/82	50

Company	Location	Start-up Date	Boiler Capacity (lb/hr) x 1000
18. Campbell Soup Co.	Salisbury, MD	/82	50
19. Boise Cascade Corp.	Kenora, Ont.	/77	45
20. Griffin Industries Ltd.	Newberry, IN	/83	40
21. East Stroudsburg State College	E. Stroudsburg, PA	/83	40
22. Abbott Laboratories	Casa Grande, AZ	/84	25
23. Providence College	Providence, RI	/84	20
24. IBM Corp.	Charlotte, NC	/80	20
25. Van Buren County Alcohol Inc.	Bonaparte, IA	/81	20
26. Power Recovery Systems Inc.	Cambridge, MA	/80	20
27. Correctional Facility	Danville, IL	/84	12
28. Nelson Industries Inc.	Fortville, IN	/84	3
29. Owen-Spencer School	Spencer, IN	/81	3

APPENDIX B
EFFECT OF PROCESS VARIABLES ON CALCIUM OXIDE CONTENT OF AFBC ASH

The quantity of calcium oxide in AFBC wastes may be different in fly ash, bed ash, and recycle fractions. Generally, it is a function of a number of variables, including:

- sulphur content of the coal,
- ash content of the coal,
- calcium carbonate content of limestone used,
- calcining efficiency,
- calcium carbonate present in coal,
- combustion efficiency (carbon utilization),
- calcium-to-sulphur ratio used,
- recycle rate,
- reaction of calcium oxide with non-sulphur species,
- combustor conditions,
- sulphur capture efficiency, and
- reaction of sulphur with non-calcium species.

The effects of some of these on the ash composition have not been quantified yet. However, an approximate estimate of calcium oxide content, averaged over fly ash, bed ash, and recycle fractions can be made by considering the sulphur content and ash content of the coal, as well as the calcium-to-sulphur ratio employed, as controllable and measurable process parameters.

For the calculations used here, it is implicitly assumed that:

- the limestone consists of 100 percent $CaCO_3$;
- the reaction, $CaCO_3 \rightarrow CaO + CO_2$, approaches completion;
- sulphur capture is exclusively by reaction with calcium oxide;
- sulphur capture efficiency is 90 percent;
- no calcium carbonate or lime-forming species are present in the coal; and
- carbon utilization approaches 100 percent.

With these premises, the following tables can be used for estimating the calcium oxide content in AFBC ash. The estimates are a function of ash and sulphur content of the coal used and calcium-to-sulphur ratio used. Note that the waste quantity is also a function of these factors. It may be estimated, using premises similar to those

used for calcium oxide content calculations. Example ash quantities for some conditions are shown in footnotes to the tables.

CALCIUM OXIDE CONTENT OF ASH

FOR COAL OF ASH CONTENT = 5%

Sulphur (%) in Coal	Ca-to-S Ratio								
	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.5	4.0
1	11[1]	14	18	21	24	27	29[3]	34	38
2	14	19	23	27	31	34	37	41	46
3	16	21	26	30	34	37	40	45	50
4	17	23	28	32	36	39	42	47	52
5	18	24	29	33	37[5]	40	43	49	53
6	18	24	29	34	38	41	44	49	54
7	19	25	30	34	38	42	45	50	54
8	19	25	30	35	39	42	45	51	55
9	19	25	31	35	39	42	46	51	55
10	20[2]	26	31	35	39	43	46[4]	51	56

1 ash quantity, kg/kg coal = 0.10
2 ash quantity, kg/kg coal = 0.54
3 ash quantity, kg/kg coal = 0.12
4 ash quantity, kg/kg coal = 0.8
5 ash quantity, kg/kg coal = 0.38

FOR COAL OF ASH CONTENT = 10%

Sulphur (%) in Coal	Ca-to-S Ratio								
	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.5	4.0
1	7[6]	10	12	15	17	19	21[8]	25	28
2	11	14	18	21	24	27	29	34	38
3	13	17	21	25	28	31	34	39	43
4	14	19	23	27	31	34	37	42	46
5	15	20	25	29	32[10]	36	39	44	48
6	16	21	26	30	34	37	40	45	50
7	17	22	27	31	35	38	41	46	51
8	17	23	28	32	36	39	42	47	52
9	18	23	28	32	36	40	43	48	52
10	18[7]	24	29	33	37	40	43[9]	49	53

6 ash quantity, kg/kg coal = 0.15
7 ash quantity, kg/kg coal = 0.59
8 ash quantity, kg/kg coal = 0.17
9 ash quantity, kg/kg coal = 0.85
10 ash quantity, kg/kg coal = 0.43

FOR COAL OF ASH CONTENT = 15%

Sulphur (%) in Coal	Ca-to-S Ratio								
	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.5	4.0
1	5[11]	7	9	11	13	15	16[13]	19	22
2	8	12	15	17	20	22	24	29	32
3	11	14	18	21	24	27	29	34	38
4	12	16	20	24	27	30	33	38	42
5	13	18	22	26	29[15]	32	35	40	44
6	14	19	23	27	31	34	37	42	46
7	15	20	24	28	32	35	38	43	48
8	16	21	25	29	33	36	39	44	49
9	16	21	26	30	34	37	40	45	50
10	16[12]	22	27	31	34	38	41[14]	46	50

11 ash quantity, kg/kg coal = 0.2
12 ash quantity, kg/kg coal = 0.64
13 ash quantity, kg/kg coal = 0.22
14 ash quantity, kg/kg coal = 0.9
15 ash quantity, kg/kg coal = 0.48

FOR COAL OF ASH CONTENT = 20%

Sulphur (%) in Coal	Ca-to-S Ratio								
	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.5	4.0
1	4[16]	6	7	9	11	12	13[18]	16	19
2	7	10	12	15	17	19	21	25	28
3	9	12	16	18	21	24	26	30	34
4	11	14	18	21	24	27	29	34	38
5	12	16	20	23	26[20]	29	32	37	41
6	13	17	21	25	28	31	34	39	43
7	14	18	22	26	30	33	35	40	45
8	14	19	23	27	31	34	37	42	46
9	15	20	24	28	32	35	38	43	47
10	15[17]	20	25	29	32	36	39[19]	44	48

16 ash quantity, kg/kg coal = 0.25
17 ash quantity, kg/kg coal = 0.69
18 ash quantity, kg/kg coal = 0.27
19 ash quantity, kg/kg coal = 0.95
20 ash quantity, kg/kg coal = 0.53